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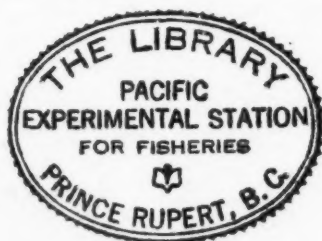
## CONTENTS

### SEC. A.—PHYSICAL SCIENCES

	Page
Water and Water-alcohol Injection in a Supercharged Jaguar Aircraft Engine— <i>M. S. Kuhring</i> - - - - -	149

### SEC. B.—CHEMICAL SCIENCES

Conductivity Data of Aqueous Mixtures of Hydrogen Peroxide and Nitric Acid— <i>W. H. Hatcher and D. W. MacLauchlan</i> -	253
The Kinetics of the Decomposition Reactions of the Lower Paraffins. II. Isobutane— <i>E. W. R. Steacie and I. E. Pudington</i> - - - - -	260
Measurement of the Dielectric Constant of Cellulose— <i>H. A. De Luca, W. Boyd Campbell and O. Maass</i> - - - - -	273



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# Canadian Journal of Research

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VOL. 16, SEC. A.

AUGUST, 1938

NUMBER 8

## **WATER AND WATER-ALCOHOL INJECTION IN A SUPERCHARGED JAGUAR AIRCRAFT ENGINE<sup>1</sup>**

BY M. S. KUHRING<sup>2</sup>

### **Abstract**

Tests have been carried out in order to determine the effect of water injection on the operation of a full-scale aircraft engine. A Jaguar Mk IV supercharged aircraft engine was used and quantities of water as great as 83 lb. per 100 lb. of fuel were injected. As would be expected, the use of water permitted large gains in power without increase in cylinder temperature and apparent detonation. An increase of approximately 90 b.hp. was obtained. Quite appreciable cooling of the air-fuel charge was noted. The specific fuel consumption remained the same or slightly better with injection. From the results it would appear that alcohol does not improve the operation of the engine appreciably, although tests were conducted only at full rich mixtures.

### **Introduction**

The take-off power of modern, high performance aircraft engines is to a very large extent limited by the octane rating of the fuel used. Should it be required to increase the take-off power of a specific engine, it will be necessary, owing to the tendency towards detonation, to use a fuel of higher octane value in order that there will not be a dangerous increase in engine temperatures.

To avoid the use of higher octane fuels or to increase the take-off power beyond that permitted by fuels at present available, the injection of certain substances such as aniline has been tried. Water injection, though tested in small laboratory and automotive engines, did not appear, from a review of the literature, to have been tried in full-scale aircraft engines, and it was considered that the subject was worthy of investigation.

### **Experimental**

The engine used was a supercharged Armstrong Siddeley Jaguar Mark IV aircraft engine. It had been employed for a recently completed program of detonation tests, and thermocouples were fitted in the temperature plug, cylinder head, and cylinder base.

Time did not permit overhauling the engine after the detonation tests, during which the engine had operated for long periods under extremely severe conditions of detonation and during which wear had doubtless occurred, and

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*Contribution from the Division of Mechanical Engineering, National Research Laboratories, Ottawa, Canada.*

<sup>2</sup> Engineer, National Research Laboratories, Ottawa.

deposits of oil had been baked on some of the cooling fins, and thus prevented adequate cooling. Consequently, there will be noted an unduly large spread in temperature of the different cylinders.

#### *Method of Injection*

The water was fed from the main under city pressure, passed through a calibrated orifice plate, and thence through copper tubing into a distance piece between the carburettor and the supercharger. The distance piece was drilled to permit the insertion of two small copper tubes which were sealed at one end and drilled in such a manner as to direct fine jets of water at the acorn nut which covers the rear end of the supercharger spindle. The water, traveling at high speed, was atomized at this point and drawn into the supercharger impeller. This arrangement is shown in Figs. 1, 2, and 3.

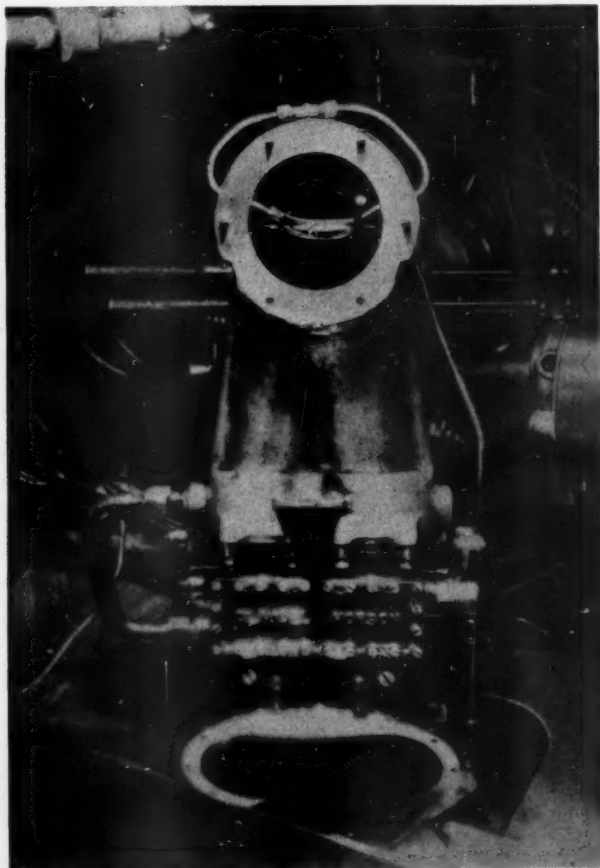


FIG. 1. *Injector unit. View looking towards injector from supercharger. Four outlet holes may be seen.*

The alcohol-water mixture was drawn from a tank and forced into the injection system by means of an electrically driven gear pump.

#### Measurements

Power was measured by means of a Heenan and Froude hydraulic dynamometer (DPRX6). (Fig. 4).



FIG. 2. *Jets being directed against piece of round bar to show degree of atomization.*

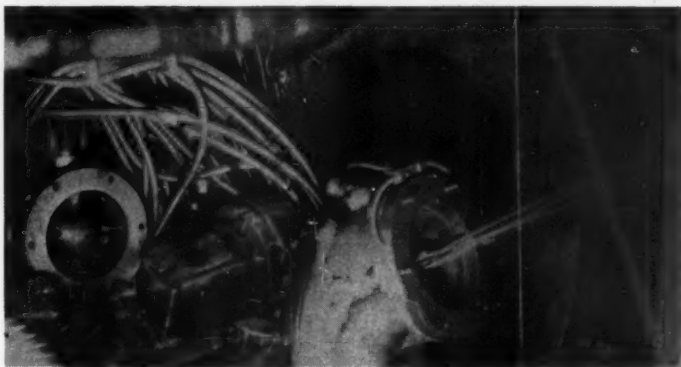


FIG. 3. *Showing water being passed from injector. The unit has been removed from the supercharger flange and turned away from the engine. The acorn nut against which the water impinges may be seen directly behind the injector unit.*

Fuel consumption was measured by means of B & B Mk IX flowmeters calibrated in Imperial pints per hour. The fuel consisted of 87 octane aviation gasoline having a specific gravity of 0.710.

The temperatures of the cylinder head, cylinder base, temperature plug, and charge were measured by means of thermocouples. Cylinder head

thermocouples were of the spark plug washer type and were fitted to the rear plug of each cylinder. Cylinder base thermocouples were screwed into the cylinder clamping ring. The Jaguar cylinders are provided with two pairs of spark plug holes so that plugs can be fitted at the front when the engine is used as either a pusher or tractor engine. During the tests, spark plugs were fitted one in front and the other at the rear of each cylinder, and temperature plugs of monel metal and stainless steel were screwed in the spare spark plug opening at the rear of each cylinder. These plugs are similar to the temperature plugs used to indicate detonation in the U.S. Army Air Corps method of octane rating of gasoline.



FIG. 4. Showing engine mounted on test bed.

The charge temperature was determined by means of a thermocouple at the tip of a stainless steel plug screwed into the induction pipe near the intake port of No. 4 cylinder, the opening normally intended for priming being used. The tip of this plug was projected well into the cylinder port in order that an accurate indication of the temperature of the charge entering the port would be obtained. Figs. 5, 6, and 7 show the thermocouples and their arrangement.

Air and oil temperatures were measured with distant reading dial thermometers.

Engine speed was determined by means of an electrical timing device which indicates the time required for 1000 revolutions of the crankshaft.

### Cooling Air

The air speed used in each experiment is given in the tables. Cowling was provided as shown in Fig. 4.

### Carburettor Air

To avoid recirculation of exhaust gases and to maintain intake air temperatures at the desired point, all air passing to the carburettor was taken from the blower duct and passed through a steam radiator. From the radiator the air was passed through a pipe into a surge box. It is in this box that temperatures were taken.

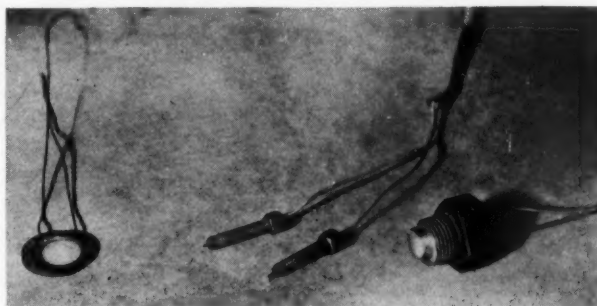


FIG. 5. Thermocouples as fitted to engine.

### Details of Engine

The engine used was an Armstrong Siddeley Jaguar Mk IV, fitted with a type E Supercharger.

Air-cooled twin row radial	Rated b.hp. at 11,500 ft. with a mani-
Dry weight, 897 lb.	fold pressure of 28.42 in. of mercury,
Number of cylinders, 14	absolute.
Bore, 5 in.	Compression ratio, 5 : 1
Stroke, 5½ in.	Carburettor, Claudel Hobson A.V.T.
Displacement, 1512 cu. in.	70E.
Normal r.p.m., 1700	Oil pressure, 65/100 lb.
Maximum r.p.m., 1870	Supercharger ratio, 12.9 : 1

Lubricating oil, Castrol R

The lubricating oil after leaving the scavenge pump passed through the carburettor and induction pipe jacket and heated the charge. This heating occurred after the air left the intake air thermometer and may have had a slight effect on the temperature of the charge entering the ports. It is considered that the effect would not be large.

### First Test

### Results

Results of the first test are shown in Table I and in Figs. 8, 9, and 10. The engine was operated on gasoline only, and readings were taken. Following this, water was injected in increasing amounts, and readings were taken until

the quantity of water injected was 60.9 lb. for each 100 lb. of fuel consumed. This was the maximum water flow possible through the equipment with the pressure then available. Following the test the engine was again operated without injection of water; the readings taken were very similar to those obtained at the start of the test.



FIG. 6. Showing thermocouples on engine.

The manifold pressure at which this test was carried out was 32.0 in. of mercury, absolute, but later tests were conducted at a manifold pressure of 35.0 in. of mercury, absolute.

In Figs. 8, 9, and 10, the results of this test are represented by triangles. It will be noted that the temperatures of the temperature plugs, cylinder head, and base are slightly lower than the corresponding figures for later tests. This is due to the lower manifold pressure at which the engine was operated.

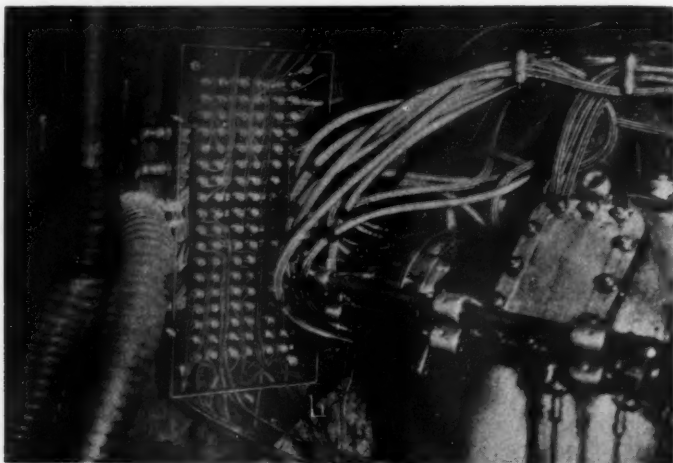


FIG. 7. Thermocouple junction box.

### Second Test

A second test was conducted to extend the range so that the optimum value could be determined. To permit more water to reach the engine the number of holes in the injection tubes was increased from four to eight and these were enlarged. Data for this test are shown in Table II and in Figs. 8, 9, and 10. In the curves the results are represented by crosses. The results are very similar to those of the first test. The ratio of water to fuel injected was less than the maximum obtained during the first test although the actual quantity of water was greater. This was due to the fact that the manifold pressure was greater and more fuel was being used.

It may be observed from the results of these two tests that the benefits obtained by water injection were still increasing at the maximum rate of injection obtained.

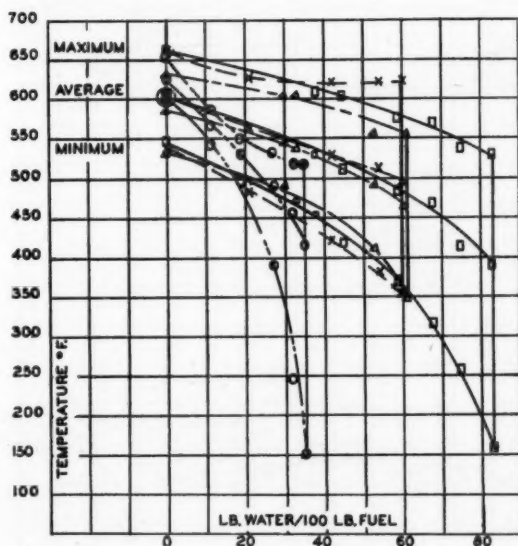


FIG. 8. Effect of varying amounts of injected water on temperature plugs.  $\Delta$ , First test;  $\times$ , second test;  $\square$ , fourth test;  $\circ$ , fifth test.

### Third Test

It was considered that advantage should be taken of the opportunity to determine the effect of a definite rate of injection of water at progressively greater throttle openings or manifold pressures.

The engine was operated without water injection at a manifold pressure of 35.0 in. of mercury. Readings were taken and water was then injected at a rate of flow which it was considered possible to maintain over quite a wide range of throttle opening. This rate of flow was maintained constant except

at one point at which it was increased for a sufficient length of time to take a set of readings (at a manifold pressure of 38.0 in. of mercury); it was then adjusted to the original rate for the remainder of the test. This point at which the rate of water flow was increased is plotted in Figs. 11, 12, and 13 as a circle, and the other points are indicated by crosses.

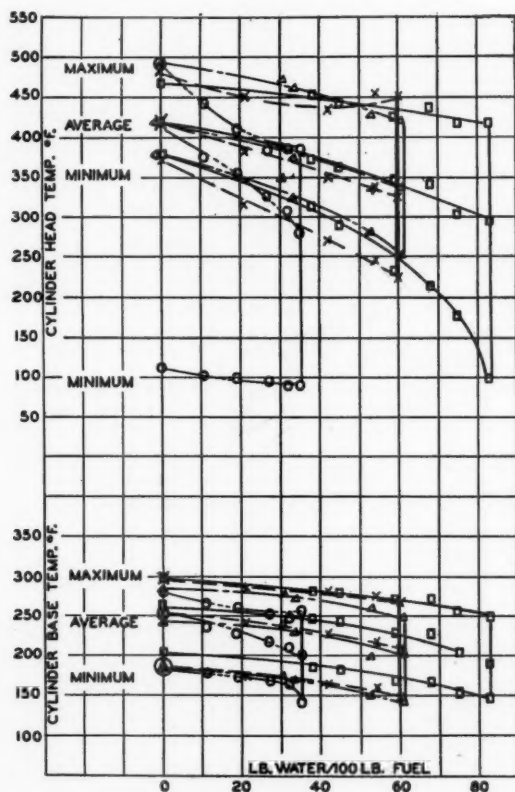


FIG. 9. Effect of varying amounts of injected water on temperatures of cylinder base and cylinder head.  $\Delta$ , First test;  $\times$ , second test;  $\square$ , fourth test;  $\circ$ , fifth test.

The throttle was opened progressively until the manifold pressure was 39.4 in. of mercury, absolute. This was as high a pressure as the super-charger would develop at full throttle opening.

Results of this test are given in Table III and Figs. 11, 12, and 13, and will be discussed later.

#### Fourth Test

In order to carry the water injection curve to a point at which the benefits secured by injection would cease, or until power would fall off, another source of water supply at a higher pressure was arranged.

The engine was operated at a manifold pressure of 35.0 in. of mercury and with increasing rates of water injection.

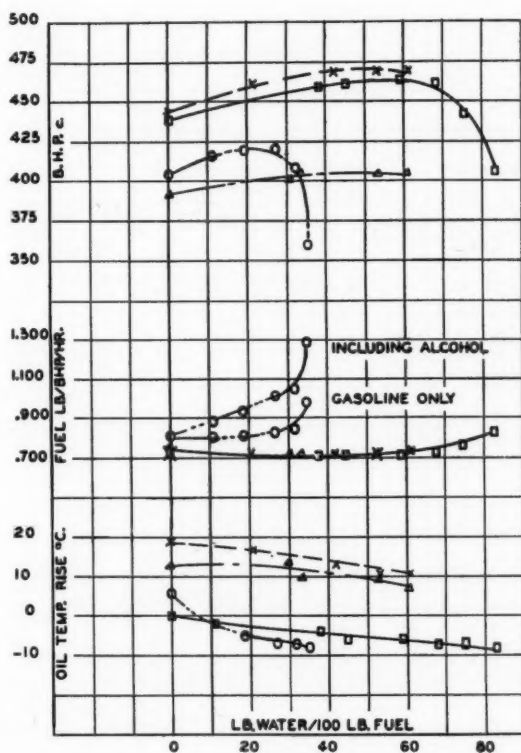


FIG. 10. Effect of varying amounts of injected water on power, fuel consumption, and heat rejected to lubricating oil. Δ, First test; ×, second test; □, fourth test; ○, fifth test.

At a flow of 83 lb. of water per 100 lb. of fuel it was definitely established that the point of maximum gain had been passed for the particular engine conditions.

Results of this test will be found in Table IV and in Figs. 8, 9, and 10. In the figures, readings are represented by squares.

*Fifth Test*

Obviously if water for injection is carried in a tank in the aircraft it is subject to freezing in the winter unless some antifreeze such as alcohol is added.

On take-off at the present time, high performance aircraft engines are operating with virtually as rich a mixture as is possible, and the addition of alcohol to the injection water, in sufficient quantities to prevent freezing, is

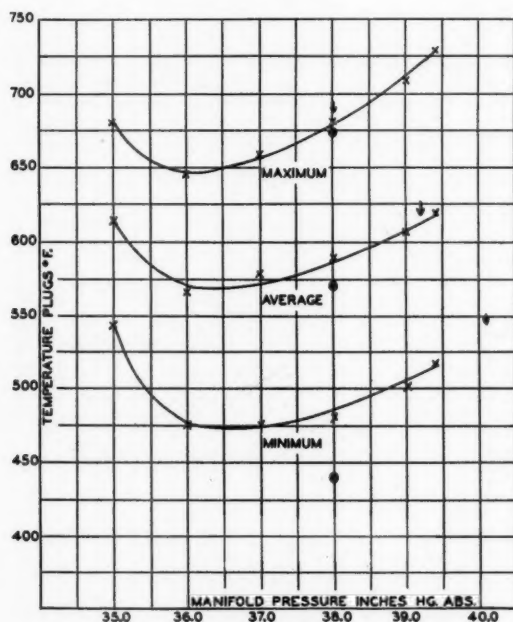


FIG. 11. Effect of constant rate of water injection on permissible manifold pressure (temperature plugs).

apt to make the mixture over rich. However, it was decided to try a mixture of water-alcohol which would be satisfactory as an antifreeze. Tests were made with a mixture containing 46.25% of alcohol by weight. The results are given in Table V and plotted, as circles in Figs. 8, 9, and 10. The specific fuel consumption is shown for gasoline alone and for both gasoline and alcohol.

### Discussions and Conclusions

The temperatures of temperature plug, cylinder head, and cylinder base tended with one exception to drop with water injection. The maximum temperatures of cylinder head and temperature plug in the second test dropped at first and then rose slightly. This is due probably to a local cylinder condition and might be ignored.

The specific fuel consumption was slightly lower with water injection up to the point at which power dropped off. All tests were conducted with the mixture control in the full rich position, including that with the alcohol-water injection. It had been hoped to obtain mixture control curves with the various degrees of water injection and particularly with the alcohol mixture, but this was not possible at the time.

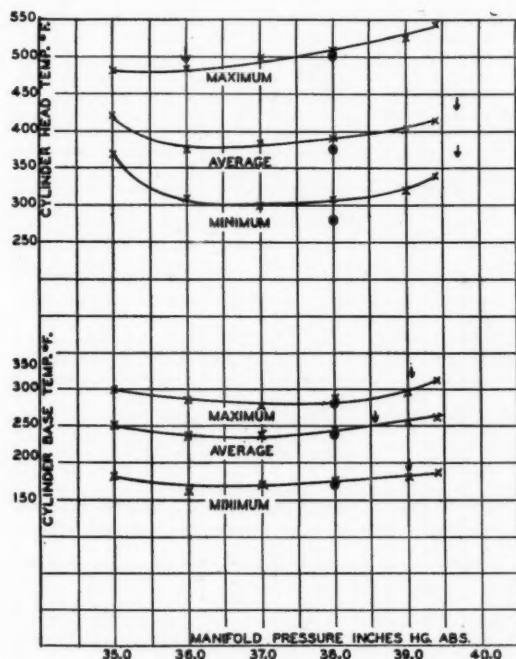


FIG. 12. Effect of constant rate of water injection on permissible manifold pressure (cylinder base and cylinder head temperatures).

The engine heat transferred to the lubricating oil, as shown by the oil temperature rise, tended to drop as water was injected, and the engine temperature decreased, in spite of the fact that power output increased.

Supercharger cooling was obviously one of the advantages of the water injection, as indicated by the charge temperature in the tables. When the engine was operating at a given manifold pressure without the water injection, and the water was then turned on, the manifold pressure, owing to the cooling effect, dropped, and the throttle had to be opened appreciably in order to maintain the given manifold pressure. This was repeated at each increase in rate of water injection. The power increase as shown in Fig. 10 gives about

25 hp. gain with water injection when the manifold pressure is maintained constant.

Figs. 11, 12, and 13 show more clearly the advantage to be derived. As stated previously, in these tests water was injected at the rate of only 35 to 37 lb. per 100 lb. of fuel. The power curve (Fig. 10) indicates that best results are obtained at a rate of flow of between 60 and 65 lb. of water per 100 lb. of fuel. This is confirmed by the better performance indicated by the single point readings taken at a manifold pressure of 38 in. with a rate of flow of

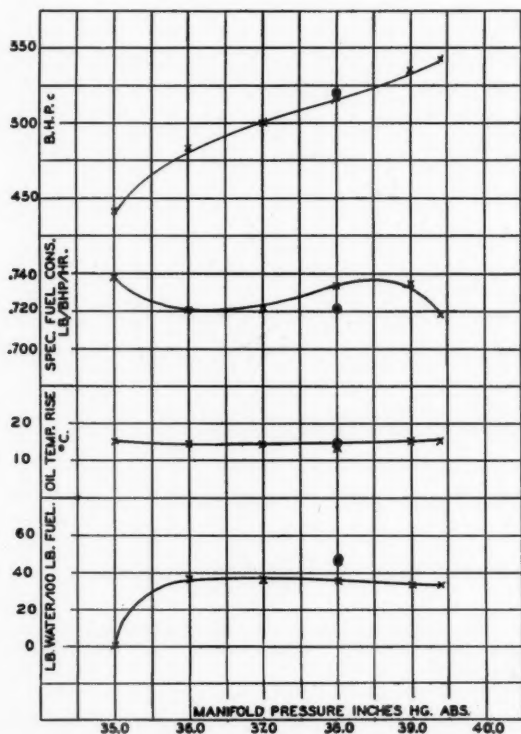


FIG. 13. Effect of constant rate of water injection on permissible manifold pressure (power, fuel consumption, and heat rejected to lubricating oil).

approximately 47 lb. per 100 lb. of fuel. Evidently the advantages gained, as shown in Figs. 11, 12, and 13 are not the maximum obtainable. Arrows placed above the curves in Figs. 11 and 12 indicate the point at which the temperatures, after dropping, increased to the values at the start, and would therefore indicate the increase in manifold pressure permissible to maintain the engine at a given temperature.

With the exception of the maximum readings, which as stated before were probably local, it would appear that with a similar rate of water injection the manifold pressure may be increased from 35.0 to 38.5 or 39.0 in. of mercury, or, expressed in horsepower, increased from 441 to 523 or 535 b.hp., a gain of 82 or 94 b.hp.

Though water injection offers an attractive method of increasing the performance of an engine at take-off and possibly even at cruising power, certain points must not be overlooked. Although sufficient water could easily be carried for take-off, a sufficient supply for cruising presents difficulties both in regard to weight and the possibility of freezing in cold weather.

From the small amount of work done in this series of tests it would appear that the use of alcohol as an antifreeze does not give the same improvement in performance as that given by water injection, although the question has not been fully examined as only one gasoline mixture strength was used.

Water recovery from the exhaust if feasible would appear to be a solution of this difficulty. There is in the exhaust an amount of water vapor roughly equal to that of the fuel consumed. In the exhaust of an engine into which water is injected at the rate of 50 lb. per 100 lb. of fuel there would be an additional 50% of water. It would then be necessary to recover from the exhaust approximately 33% of the water vapor for injection. The exhaust temperature, though not measured, is probably considerably lower with water injection, and this would favor water recovery. Water recovery from the exhaust has been used on airships but the necessary equipment might be too cumbersome for aeroplanes.

As pointed out previously, the fuel used was 87 octane gasoline containing lead tetraethyl, and it was found, at the end of virtually all the test runs, that the spark plugs were on the verge of failure. Some of the spark plugs failed before the end of the tests owing to the building up of a deposit on the insulator. It would appear from this that the lead, instead of being carried out of the combustion chamber in the form of a vapor, was being deposited in the combustion chamber and thus fouled the plugs. Hotter running plugs might improve operation but would not prevent the deposit from covering the combustion chamber.

Heavy deposits were found on the tops of the pistons. Over large areas of the piston, carbon had flaked off, and it is quite possible that this carbon caused pre-ignition at times, particularly during the last run, when the tests were concluded owing to irregular operation of one and possibly more of the cylinders.

Examination of the engine after the test showed cylinders and pistons to be in exceptionally good condition. Further tests with a non-leaded fuel should be carried out to determine whether it was the deposition of lead which caused the spark plugs to fail, or whether carbon alone would cause failure. Such tests would also indicate to what extent water injection in the engine could be used to replace at least some of the lead in a fuel.

TABLE I  
WATER INJECTION TESTS

Engine started 11.23 a.m., off 11.53 a.m.; started 3.20 p.m., off 5.22 p.m.  
Cold junction, 62° F. Barometer, 29.85 in. of mercury. Sp. gr. of fuel, 0.710. Velocity of cooling air, 123 m.p.h. past cylinder heads

Time	4.20*	4.40**	4.44	4.49	4.52	4.55	4.58	5.02	5.05	5.08	5.10	5.13
Water flow in. of Hg	—	—	1.56	1.81	1.88	4.75	4.75	6.25	6.25	—	—	—
lb./hr.	—	—	88	96	98	156	156	179	179	—	—	—
lb./100 lb. fuel	—	—	30.5	32.9	33.6	52.9	53.0	60.9	60.9	—	—	—
Fuel pints/hr.(FM)	—	323	325	329	329	332	331	331	331	—	324	322
lb./b.hp./hr.(FM)	—	0.746	0.732	0.732	0.732	0.739	0.737	0.737	0.735	—	0.745	0.746
R.p.m.	—	1702	1710	1702	1704	1699	1699	1697	1699	—	1694	1701
B.h.p.	—	384	394	398	399	399	399	399	400	—	386	383
B.h.p.	—	391	401	404	405	405	405	404	404	—	390	390
Manifold press., in. of Hg	32.0	32.1	31.8	32.0	31.9	31.9	32.0	32.0	31.9	—	32.0	32.0
Intake air, °F.	—	80	78	77	77	76	75	73	70	—	70	70
Charge temp., °C.	—	142	112	107	107	103	98	94	94	—	129	133
Cooling air, °F.	—	46	46	46	47	47	47	47	47	—	47	47
Oil	—	75	75	75	75	75	75	75	74	—	75	75
Press.	—	61	61	62	62	62	62	62	61	—	61	61
Inlet press.	—	73	74	73	72	72	71	70	69	—	71	71
Outlet press.	—	12	13	11	10	10	9	8	8	—	8	10
Temp. rise, °F.	—	371	364	326	322	307	281	270	258	—	364	382
Cylinder head, °F.	—	378	368	357	354	343	329	326	314	—	368	375
1†	—	382	368	361	354	333	322	311	300	—	378	385
2	—	430	406	392	389	371	361	347	336	—	420	433
3	—	413	382	364	361	329	314	304	304	—	403	410
4	—	464	447	444	433	410	403	399	399	—	457	460
5	—	403	382	382	375	361	354	354	354	—	385	385
6	—	—	—	—	—	—	—	—	—	—	—	—
7	—	—	—	—	—	—	—	—	—	—	—	—

Table continued on page 163.

TABLE I—Continued  
 WATER INJECTION TESTS

Time		4.20*	4.40**	4.44	4.49	4.52	4.55	4.58	5.02	5.05	5.08	5.10	5.13
Cylinder head, °F.—Contc.													
8		—	490	471	460	460	444	430	430	420	—	477	487
9		—	406	389	385	385	368	361	350	347	—	406	406
10		—	447	392	385	385	350	343	329	326	—	433	437
11		—	396	350	343	340	314	307	300	296	—	389	389
12		—	430	389	364	361	289	285	262	251	—	423	430
13		—	406	368	347	343	285	281	262	258	—	399	399
14		—	413	375	368	368	333	329	311	307	—	406	406
1		—	378	340	326	326	281	281	258	258	—	382	382
Av.		—	416	389	377	374	346	336	325	337	—	408	413
Max.		—	490	471	460	460	444	430	430	420	—	477	487
Min.		—	371	350	326	322	281	281	258	251	—	364	375
Cylinder base, °F.													
1		—	225	225	211	211	201	193	186	176	—	208	220
2		—	251	248	243	241	239	232	229	220	—	237	245
3		—	239	235	227	225	220	211	208	201	—	222	232
4		—	263	263	253	253	243	248	235	227	—	251	265
5		—	243	239	229	229	211	201	196	183	—	235	241
6		—	248	253	243	243	239	235	239	235	—	243	251
7		—	211	211	211	211	203	201	201	201	—	211	211
8		—	243	235	229	227	225	218	216	211	—	227	235
9		—	286	277	277	272	263	260	253	248	—	277	283
10		—	263	253	248	243	235	227	216	208	—	201	258
11		—	186	171	166	166	153	150	142	140	—	171	176
12		—	263	253	243	243	211	206	191	181	—	251	263
13		—	243	235	222	220	186	183	176	168	—	235	239
14		—	258	243	241	239	225	220	211	203	—	248	255
Av.		—	244	241	232	230	218	199	207	200	—	230	241
Max.		—	286	277	277	272	263	260	253	248	—	277	283
Min.		—	186	171	166	166	153	150	142	140	—	171	176

Table concluded on page 164.

TABLE I—*Concluded*  
WATER INJECTION TESTS

Engine started 11.23 a.m., off 11.53 a.m.; started 3.20 p.m., off 5.22 p.m.  
Cold junction, 62° F. Barometer, 29.85 in. of mercury. Sp. gr. of fuel, 0.710. Velocity of cooling air, 123 m.p.h. past cylinder heads

Time	4.20*	4.40**	4.44	4.49	4.52	4.55	4.58	5.02	5.05	5.08	5.10	5.13
Temperature plugs, °F.												
1	—	531	490	471	467	450	413	399	378	—	528	538
2	—	563	528	525	519	503	490	477	467	—	554	557
3	—	585	547	541	538	506	490	474	457	—	585	591
4	—	585	550	541	538	509	500	480	471	—	588	591
5	—	544	500	474	471	450	413	392	371	—	538	538
6	—	630	603	603	597	566	557	557	554	—	627	627
7	—	621	575	575	575	554	547	544	547	—	606	603
8	—	618	588	588	588	560	554	547	541	—	612	618
9	—	585	560	557	554	525	516	503	503	—	585	585
10	—	603	550	541	538	497	484	460	460	—	603	603
11†	—	585	538	516	516	440	413	357	347	—	579	588
12	—	582	538	535	535	497	490	467	464	—	582	582
13†	—	586	547	539	536	505	489	471	463	—	582	585
Max.	—	630	603	603	597	566	557	557	554	—	627	627
Min.	—	531	490	471	467	440	413	357	347	—	528	538

\*No water. \*\*Water turned on after readings were taken. †Cylinder number. ‡ Out of order.

TABLE II  
WATER INJECTION TESTS

 Engine started 3.00 p.m., off 5.37 p.m.; restarted 6.03 p.m., off 6.41 p.m.  
Cold junction, 52° F. Barometer, 30.25 in. Hg. Sp. gr. of fuel, 0.710. Velocity of cooling air, 119 m.p.h. (at 32° F.).

Time	3.42*	3.45*	3.48**	3.49	3.53	3.56	4.00	4.05	4.09	4.13	4.16	4.21
Water flow in. Hg.	—	—	—	1	1	3.69	3.75	6.13	6.50	7.88	7.94	7.75
lb./hr.	—	—	—	70	70	139	140	177	182	202	203	201
lb./100 lb. fuel	—	—	—	21.6	21.3	42.0	41.9	52.8	54.3	59.9	60.4	59.6
Fuel	—	—	—	—	—	—	—	—	—	—	—	—
gals/hr. (FM)	355	357	—	365	370	373	376	377	377	380	378	379
lb./b.hp./hr. (FM)	0.728	0.729	—	0.717	0.720	0.718	0.724	0.723	0.723	0.727	0.722	0.722
R.p.m.	1692	1700	—	1701	1694	1702	1696	1689	1700	1702	1701	1701
B.hp.	433	435	—	452	455	461	461	463	463	464	465	465
B.hp.	441	443	—	459	462	468	468	470	469	470	470	470
Manifold press., in. of Hg	35.0	35.0	—	34.8	35.0	34.9	35.0	34.9	35.0	35.0	35.0	35.0
Intake air, °F.	79	78	—	77	76	75	75	75	74	74	72	72
Charge temp., °F.	123	123	—	97	93	88	88	88	88	84	84	84
Oil	—	—	—	—	—	—	—	—	—	—	—	—
Press.	76.5	76.5	—	76.5	76.5	76.5	76.5	76.5	76.5	76.5	76.5	77
Inlet press.	37	38	—	37	40	43	43	43	43	43	43	43
Outlet press.	56	57	—	57	57	56	56	55	54	54	54	53
Temp. rise, °F.	19	19	—	20	17	13	13	12	11	11	11	10
Cylinder head, °F.	—	—	—	—	—	—	—	—	—	—	—	—
1	372	372	—	361	316	286	271	248	248	233	225	241
2	382	382	—	372	358	344	330	319	304	312	304	308
3	379	379	—	372	354	333	326	308	308	297	290	290
4	443	443	—	427	410	396	389	379	379	372	368	361
5	416	416	—	396	365	337	326	308	308	301	290	297
6	483	483	—	457	450	434	434	430	434	434	434	437
7	389	396	—	379	375	365	365	361	354	358	354	351
8	454	454	—	416	413	407	400	447	454	454	450	443

Table continued on page 166.

TABLE II—Continued  
WATER INJECTION TESTS

Engine started 3.00 p.m., off 5.37 p.m.; restarted 6.03 p.m., off 6.41 p.m.  
Cold junction, 52° F. Barometer, 30.25 in. Hg. Sp. gr. of fuel, 0.710. Velocity of cooling air, 119 m.p.h. (at 32° F.).

Time	3.42*	3.45*	3.48**	3.49	3.53	3.56	4.00	4.05	4.09	4.13	4.16	4.21
Cylinder head, *F.—Conte.												
9	400	403	—	393	389	372	368	354	354	354	351	347
10	440	443	—	416	416	389	389	368	368	375	358	361
11	396	400	—	358	358	333	340	323	326	323	308	312
12	443	440	—	400	389	319	312	282	290	267	271	271
13	393	396	—	358	347	282	282	248	260	244	244	248
14	410	416	—	386	389	354	347	323	326	308	301	316
1	372	372	—	319	319	271	271	241	248	225	229	241
Av.	414	416	—	392	381	354	349	336	338	331	325	320
Max.	483	483	—	457	450	434	434	447	454	454	450	443
Min.	372	372	—	361	316	282	271	248	248	233	225	241
Cylinder base, *F.												
1	235	235	—	235	241	206	197	181	178	176	171	171
2	258	258	—	255	253	241	237	229	227	227	220	220
3	237	239	—	239	229	220	218	208	206	206	201	198
4	269	272	—	272	260	258	253	248	245	243	243	248
5	258	248	—	272	260	232	216	203	203	193	191	191
6	274	295	—	272	272	216	206	208	208	206	206	263
7	220	220	—	220	216	211	206	208	208	206	206	†
8	239	239	—	235	229	235	225	225	225	225	222	220
9	279	286	—	291	286	281	281	269	274	274	269	267
10	267	263	—	255	258	251	248	237	241	235	232	232
11	186	186	—	173	173	166	163	158	158	156	147	147
12	267	267	—	260	253	251	225	198	203	186	186	188
13	243	245	—	245	225	220	191	173	173	168	168	168
14	265	267	—	255	251	237	235	216	218	206	201	211
Av.	250	251	—	246	241	233	226	216	216	212	209	210
Max.	279	295	—	291	286	281	281	277	274	274	269	267
Min.	186	186	—	173	173	166	163	150	158	156	147	147

Table concluded on page 167.

TABLE II—Concluded  
 WATER INJECTION TESTS

Engine started 3.00 p.m., off 5.37 p.m.; restarted 6.03 p.m., off 6.41 p.m.  
 Cold junction, 52° F. Barometer, 30.25 in. Hg. Sp. gr. of fuel, 0.710. Velocity of cooling air, 119 m.p.h. (at 32° F.).

Time	3.42*	3.45*	3.48**	3.49	3.53	3.56	4.00	4.05	4.09	4.13	4.16	4.21
Temperature plugs, °F.												
1	540	540	—	502	480	437	420	379	382	354	354	368
2	581	584	—	553	547	521	512	493	496	483	487	487
3	584	590	—	559	556	534	521	493	499	474	474	474
4	587	605	—	572	569	556	544	534	534	525	521	518
5	562	562	—	499	496	450	440	416	420	400	396	396
6	656	662	—	626	626	611	620	620	620	626	626	626
7	605	605	—	575	575	569	565	562	559	559	559	559
8	623	626	—	596	596	590	590	605	611	602	596	593
9	602	602	—	575	578	553	553	540	540	528	525	525
10	623	626	—	587	590	562	562	544	547	537	521	531
11†			—	559	559	470	470	423	430	372	400	407
12			—	565	575	534	537	499	509	487	483	490
13†			—	564	562	532	528	509	512	496	495	498
Av.	598	602	—	626	626	611	620	620	620	626	626	626
Max.	656	662	—	499	480	437	420	379	382	354	354	368
Min.	540	540	—									

\* No water.

\*\* Water turned on after readings were taken.

† Out of order.

TABLE III  
WATER INJECTION TESTS

Engine started, 3.00 p.m., off, 5.37 p.m.; restarted, 6.03 p.m., off, 6.41 p.m.  
Cold junction, 52° F. Barometer, 30.25 in. of mercury. Sp. gr. of fuel, 0.710. Velocity of cooling air, 119 m.p.h. (at 32° F.)

Time	4.30*	4.33**	4.55	4.58	5.02	5.05	5.09	5.13	5.16	5.20	5.23	5.26	5.29
Water flow in. of Hg	—	—	3.25	3.13	3.13	3.25	6.0	3.13	3.44	3.38	3.19	3.19	3.13
lb./hr.	—	—	131	128	128	131	175	128	134	133	129	129	128
lb./100 lb. fuel	—	—	37.8	37.1	36.3	36.7	47.4	34.4	35.9	34.7	33.5	34.1	33.5
Fuel pints/hr.(FM)	364	362	391	388	398	402	416	419	420	431	434	426	430
lb./b.hp./hr.(FM)	0.740	0.738	0.728	0.721	0.711	0.721	0.730	0.730	0.733	0.732	0.734	0.716	0.718
R.p.m.	1701	1696	1707	1708	1706	1702	1697	1702	1701	1691	1700	1689	1701
B.hps.	437	436	477	478	497	495	512	510	509	523	525	528	532
B.hps.	442	441	482	483	502	501	520	518	518	533	535	539	543
Manifold press., in. of Hg	35.0	35.0	36.0	36.0	37.0	37.0	38.0	33.0	38.0	39.0	39.0	39.4	39.4
Intake air, °F.	72	71	72	71	71	73	76	77	78	79	80	82	83
Charge temp., °F.	119	123	88	88	88	93	93	97	97	97	97	97	97
Oil													
Press.	77	77	77	77	77	77	77	77	77	77	77	76	76
Inlet press.	42	41	39	41	43	44	45	45	47	47	46	47	47
Outlet press.	55	56	52	55	58	58	59	60	60	61	61	62	62
Temp. rise, °F.	13	15	13	14	15	14	14	15	13	14	15	15	15
Cylinder Head, °F.													
1	368	368	368	368	316	308	297	308	308	319	319	333	337
2	386	386	344	347	351	351	347	354	361	361	365	375	382
3	382	389	344	344	351	347	340	351	358	358	361	372	379
4	447	450	389	393	416	420	423	437	427	430	434	437	440
5	423	423	344	344	361	365	368	389	386	393	396	396	400
6	477	480	447	447	464	461	464	477	477	483	487	496	502
7	382	386	358	358	361	361	358	361	368	372	379	379	382

Table continued on page 169.

TABLE III—Continued  
WATER INJECTION TESTS

 Engine started 3.00 p.m., off, 5.37 p.m.; restarted, 6.03 p.m., off, 6.41 p.m.  
Cold junction, 52° F. Barometer, 30.25 in. of mercury. Sp. gr. of fuel, 0.710. Velocity of cooling air, 119 m.p.h. (at 32° F.).

Time	4.30*	4.33**	4.55	4.58	5.02	5.05	5.09	5.13	5.16	5.30	5.23	5.26	5.29
Cylinder Head, °F.—Contc.													
8	499	502	477	483	496	496	502	512	509	525	525	537	544
9	403	403	375	379	396	393	379	393	396	400	403	403	410
10	457	454	423	430	440	437	410	430	420	430	437	443	450
11	393	400	319	326	372	368	358	368	358	372	375	379	386
12	443	440	347	351	347	351	330	361	372	372	375	389	393
13	403	400	308	308	294	297	279	326	326	330	340	358	361
14	416	416	393	396	407	403	368	410	403	413	416	427	423
1	368	368	308	308	316	308	275	312	304	319	326	333	337
Av.	420	421	370	372	384	383	373	391	391	394	401	409	414
Max.	499	480	477	483	496	496	502	512	509	525	525	537	544
Min.	368	368	308	308	294	297	279	308	308	319	319	333	337
Cylinder base, °F.													
1	229	235	211	216	218	220	216	220	225	229	235	239	243
2	253	255	239	241	245	248	251	253	255	255	260	263	267
3	235	239	220	225	227	229	229	232	237	237	239	243	248
4	267	272	248	253	260	263	274	272	269	272	274	293	293
5	201	196	216	220	227	232	235	243	241	243	248	253	258
6	281	286	281	286	293	279	281	289	289	291	295	309	314
7†													
8	243	245	235	237	241	243	248	248	251	255	258	263	263
9	297	300	286	277	281	†	267	269	267	277	279	281	283
10	265	267	253	258	263	263	171	173	176	177	181	181	186
11	183	183	161	163	173	173	171	173	176	177	181	181	186
12	267	269	239	241	251	253	245	255	258	265	279	274	277
13	248	248	208	213	201	206	196	220	225	237	235	243	248
14	260	263	248	251	258	258	245	260	258	265	267	272	272
Av.	248	251	234	237	241	239	238	245	246	249	254	259	262
Max.	297	300	286	286	293	279	281	289	289	291	295	309	314
Min.	183	183	161	163	173	173	171	173	176	178	181	181	186

Table concluded on page 170.

TABLE III—*Concluded*  
WATER INJECTION TESTS

Engine started 3.00 p.m., off, 5.37 p.m.; restarted, 6.03 p.m., off, 6.41 p.m.  
Cold junction, 52° F. Barometer, 30.25 in. of mercury. Sp. gr. of fuel, 0.710. Velocity of cooling air, 119 m.p.h. (at 32° F.).

Time	4.30*	4.33**	4.55	4.58	5.02	5.05	5.09	5.13	5.16	5.30	5.23	5.26	5.29
Temperature plugs, °F.													
1	544	544	474	474	490	477	440	493	480	496	502	512	518
2	599	596	537	544	550	553	537	562	565	572	575	587	593
3	611	611	556	559	562	559	534	569	572	581	593	599	608
4	620	620	559	562	584	587	587	608	602	608	608	608	617
5	572	572	477	480	506	509	499	534	531	547	544	544	544
6	677	680	641	647	665	659	674	680	680	701	709	723	729
7	602	605	569	575	593	593	599	602	599	614	620	626	629
8	659	656	638	638	656	656	665	677	674	696	696	712	717
9	599	602	569	569	584	587	584	593	590	599	602	611	611
10	641	641	605	608	620	620	611	608	608	629	629	644	647
11†		629	531	534	537	537	531	553	556	565	569	587	587
12													
13†		614	593	596	608	602	599	605	602	517	626	635	635
14													
Av.	614	614	582	566	580	578	572	590	588	602	606	616	620
Max.	677	680	641	647	665	659	674	680	680	701	709	723	729
Min.	544	544	474	474	490	477	440	493	480	496	502	512	518

\* No water.

\*\* Water turned on after readings were taken.

† Out of order.

TABLE IV  
WATER INJECTION TESTS

Engine started, 9.35 a.m. Barometer, 30.3 in. of mercury. Sp. gr. of fuel, 0.710. Oil heater on throughout test. Ethyl aviation gasoline, 87 octane number. CFR motor method

Time	10.08*	10.11*	10.18**	10.24	10.27	10.30	10.35	10.37	10.41	10.43	10.46	10.51	10.54	10.58	11.03
Water flow lb./hr.	—	—	—	120	120	144	144	191	193	221	221	247	247	273	273
lb./100 lb. fuel	—	—	—	38	38	45	45	59	59	68	68	76	75	85	83
Fuel pints/hr.(FM)	351	348	352	358	360	363	364	364	366	368	366	369	372	364	368
lb./b.hp./hr.(FM)	0.737	0.734	0.736	0.714	0.720	0.718	0.725	0.733	0.725	0.732	0.728	0.765	0.774	0.779	0.834
R.p.m.	1696	1690	1693	1704	1697	1697	1690	1682	1696	1699	1698	1696	1704	1685	1682
B.h.p.	424	422	425	446	445	449	447	442	449	446	447	429	428	416	393
B.h.p.	438	436	439	461	460	464	462	457	464	461	462	443	442	430	406
Manifold press., in. of Hg	35.0	35.0	35.0	35.0	34.9	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0
Intake air, °F.	99	99	97	97	97	97	97	97	97	97	96	95	95	95	95
Charge temp., °F.	138	133	138	107	107	103	103	98	103	98	98	98	98	98	98
Cooling air, °F., (at 112 m.p.hr.)	36	36	36	36	36	36	36	36	36	36	36	36	36	36	36
Oil Press.	77	76	75	75	75	75	74	74	74	74	74	74	75	75	75
Inlet press.	53	54	55	58	59	59	59	59	58	58	58	58	57	56	56
Outlet press.	57	57	55	55	55	54	53	52	52	52	51	51	50	49	48
Temp. rise, °F.	4	3	0	-3	-4	-5	-6	-7	-6	-6	-7	-7	-7	-7	-8
Cylinder head, °F.	382	382	378	326	322	307	311	285	281	285	277	258	254	251	251
1	396	399	396	364	361	350	354	333	340	340	333	311	304	300	289
2	389	389	389	361	361	350	354	322	329	326	322	285	277	281	262
3	433	433	426	389	389	375	378	350	350	350	347	285	292	318	314
4	430	430	426	357	361	350	354	392	418	411	407	285	292	318	292
5	464	464	457	413	410	410	410	392	403	413	413	396	396	396	389
6	423	423	413	365	389	382	385	375	382	378	378	364	357	371	375
7	421	424	467	457	453	447	444	433	427	440	437	426	417	410	417

Table continued on page 172.

TABLE IV—Continued  
WATER INJECTION TESTS

Engine started, 9.35 a.m. Barometer, 30.3 in. of mercury. Sp. gr. of fuel, 0.710. Oil heater on throughout test. Ethyl aviation gasoline, 87 octane number. CFR motor method.

Time	10.08*	10.11*	10.18**	10.24	10.27	10.30	10.35	10.37	10.41	10.43	10.46	10.51	10.54	10.58	11.03
Cylinder head, °F.—Contc.															
9	403	406	406	382	385	378	378	364	371	371	368	350	343	336	343
10	437	440	437	368	368	361	361	333	343	329	333	318	311	307	314
11	406	410	413	364	361	354	354	340	343	343	326	326	322	322	326
12	450	450	447	357	357	340	333	300	300	277	270	176	204	204	98
13	385	389	382	307	314	292	289	215	228	215	180	180	176	164	164
14	420	423	423	371	371	368	364	336	350	343	311	300	300	300	300
1	382	—	378	322	322	311	311	277	289	281	277	254	254	247	247
Av.	417	419	419	372	372	362	362	335	348	345	341	308	304	305	295
Max.	464	464	467	457	453	447	444	433	427	440	437	426	417	410	417
Min.	382	382	378	307	314	292	289	215	228	215	215	176	176	176	98
Cylinder base, °F.															
1	245	247	242	232	228	221	221	210	204	206	202	188	178	178	173
2	263	265	260	255	251	249	251	265	251	260	255	234	223	223	196
3	245	249	247	245	240	234	234	228	226	223	223	204	196	193	183
4	281	283	279	273	268	260	260	253	247	251	249	237	228	221	210
5	263	263	260	234	234	232	234	212	212	210	208	240	186	183	181
6	306	301	298	281	275	275	277	273	279	277	268	265	255	226	218
7	249	249	245	234	234	230	230	226	223	226	226	221	218	215	212
8	296	298	293	286	283	279	279	279	270	275	273	265	255	253	249
9	277	273	263	263	263	251	251	245	240	245	238	232	221	†	†
10	273	277	277	255	255	263	268	240	249	242	237	215	210	210	202
11	196	199	204	188	186	183	183	166	168	168	166	155	152	152	149
12	268	263	260	240	237	230	232	237	206	196	191	171	166	168	146
13	258	255	253	226	228	212	212	181	183	183	181	171	168	168	163
14	263	263	263	245	245	242	240	221	228	226	223	202	196	188	181
Av.	263	263	260	247	245	240	241	231	228	228	226	214	204	198	189
Max.	306	301	298	286	283	279	279	279	279	277	273	265	255	253	249
Min.	196	199	204	188	186	183	183	166	168	168	166	155	152	152	146

Table concluded on page 173.

TABLE IV—Concluded  
WATER INJECTION TESTS

Engine started, 9.35 a.m. Barometer, 30.3 in. of mercury. Sp. gr. of fuel, 0.710. Oil heater on throughout test. Ethyl aviation gasoline, 87 octane number. CFR motor method.

Time	10.08*	10.11*	10.18**	10.24	10.27	10.30	10.35	10.37	10.41	10.43	10.46	10.51	10.54	10.58	11.03
Temperature plugs, °F.															
1	550	550	544	471	467	453	453	403	417	497	†				
2	594	594	591	544	541	535	535	490	512	506	500	444	440	440	417
3	609	612	612	560	557	547	547	493	519	500	497	417	417	426	385
4	615	615	612	557	557	547	547	497	512	512	509	467	467	467	460
5	606	603	597	493	497	490	484	392	444	417	413	361	385	378	382
6	660	663	660	†											
7	603	603	594	544	544	487	480	†	575	575	569	541	538	528	528
8	660	663	657	612	609	603	603	563	512	547	531	493	484	480	487
9	615	609	609	569	569	566	563	512	487	474	474	450	440	433	444
10	588	591	588	525	512	519	509	464	484	474	467	440	440	437	440
11	585	588	588	503	509	503	503	467	484	474	396	270	274	270	159
12	642	539	633	535	531	512	512	426	450	396	318	254	254	247	224
13	550	554	563	440	453	426	417	343	368	322	318	254	258	247	224
14	563	563	563	519	516	506	503	484	497	480	474	426	426	406	368
Av.	603	603	601	529	528	515	512	461	484	474	468	415	415	410	390
Max.	610	663	660	612	609	603	603	563	575	575	569	541	538	528	528
Min.	550	554	544	471	453	426	417	392	368	322	318	254	258	247	159

Before the engine was stopped, it was found that with the water injection off, the power had fallen off and the consumption of fuel had risen rapidly 400 pints per hr. This was later found to be due to fouled spark plugs and a loose induction pipe.

During the readings at 10.58 the vibration of the engine became excessive and was still greater when the 11.03 readings were taken.

\* No water.

\*\* Water turned on after readings were taken.

† Out of order.

TABLE V  
WATER AND ALCOHOL INJECTION TESTS

Alcohol 46½% of water/alcohol blend by weight. Engine started, 3.15 p.m. Barometer, 29.90 in. of mercury. Sp. gr. of fuel, 0.710

Time	3.27*	3.30**	3.35	3.43	3.47	3.49	3.51	3.54	3.59	4.01	4.05
Pints fuel/hr.(FM)	354	354	357	364	370	370	375	380	379	374	388
Fuel only, lb./b.hp./hr.(FM)	0.818	0.814	0.802	0.808	0.813	0.813	0.826	0.833	0.842	0.842	0.989
Alcohol and fuel, lb./b.hp./hr.	0.818	0.814	0.878	0.882	0.940	0.940	1.015	1.020	1.060	1.071	1.285
Lb./hr. alcohol and water	—	—	66	66	114	114	167	167	197	197	226
Lb. water/100 lb. fuel	—	—	11	11	19	19	27	27	32	32	35
Lb. alcohol/100 lb. fuel	—	—	10	9	16	16	23	23	27	27	30
R.p.m.	1704	1707	1697	1699	1701	1697	1691	1701	1704	1696	1700
B.h.p.	385	387	396	401	405	405	404	406	401	395	349
B.h.p.	401	403	411	416	420	419	418	420	415	408	360
Manifold press., in. of Hg	35.0	35.0	34.9	35.0	35.0	35.0	34.9	35.0	35.1	35.0	35.0
Intake air, °F.	104	104	102	100	99	98	98	98	97	97	97
Charge temp., °F.	138	138	112	107	103	103	98	94	94	94	94
Cooling air, °F. (at 112 m.p.hr.)	38	38	38	37	37	37	37	37	37	37	37
Oil											
Press.	77	77	77	77	77	77	76	76	76	76	76
Inlet press.	40	42	48	49	52	52	52	53	53	53	53
Outlet press.	50	48	47	47	47	47	47	46	45	46	45
Temp. rise, °F.	10	6	-1	-2	-5	-5	-5	-7	-8	-7	-8
Cylinder head, °F.											
1	399	403	380	371	361	350	333	322	304	300	266
2	392	392	378	364	354	350	336	322	304	300	270
3	406	406	392	371	361	357	337	326	304	300	266
4	450	453	430	417	403	396	378	375	368	350	350
5	426	423	403	389	375	364	350	343	326	326	292
6†											
7	444	444	420	399	385	375	364	371	371	368	361

Table continued on page 175.

TABLE V—Continued  
 WATER AND ALCOHOL INJECTION TESTS

Alcohol 46½% of water/alcohol blend by weight. Engine started, 3.15 p.m. Barometer, 29.90 in. of mercury. Sp. gr. of fuel, 0.710

Time	3.27*	3.30**	3.35	3.43	3.47	3.49	3.51	3.54	3.59	4.01	4.05
Cylinder head, °F.—Contc.											
8	112	112	103	103	98	98	94	94	89	89	89
9	433	433	423	399	399	399	385	385	385	385	385
10	490	490	460	444	413	410	382	371	371	371	368
11	426	426	403	396	375	375	357	354	371	371	340
12	457	457	420	406	368	364	311	304	277	277	212
13	444	444	403	392	361	354	281	277	231	196	89
14	457	457	433	426	413	406	392	389	371	371	343
1	403	403	382	371	354	354	322	322	300	300	266
Av.	410	411	388	375	311	354	330	326	313	309	279
Max.	490	490	460	444	413	410	385	385	385	385	385
Min.	112	112	103	103	98	98	94	94	89	89	89
Cylinder base, °F.											
1	240	245	242	232	230	228	226	215	210	208	191
2	258	265	260	253	249	247	242	237	228	230	215
3	245	249	247	237	234	232	228	223	212	212	196
4	275	281	279	265	263	260	253	251	247	247	237
5	273	273	263	247	245	242	234	232	223	223	255
6†											
7	228	237	230	230	221	226	218	221	210	210	210
8	178	183	181	176	173	173	168	166	163	163	161
9	251	253	258	247	237	234	228	228	226	226	234
10	277	281	268	258	255	249	234	232	193	232	221
11	206	206	199	193	188	186	176	171	166	166	161
12	258	263	258	240	228	226	218	210	206	202	163
13	270	275	258	251	240	234	206	202	181	173	140
14	268	270	263	258	249	247	240	237	232	228	210
Av.	248	252	247	237	232	230	220	217	207	209	200
Max.	277	281	279	265	263	260	253	* 251	247	247	255
Min.	178	183	181	176	173	173	168	166	163	163	140

Table concluded on page 176.

TABLE V—*Concluded*  
WATER AND ALCOHOL INJECTION TESTS

Alcohol 46½% of water/alcohol blend by weight. Engine started, 3.15 p.m. Barometer, 29.90 in. of mercury. Sp. gr. of fuel, 0.710

Time	3.27*	3.30**	3.35	3.43	3.47	3.49	3.51	3.54	3.59	4.01	4.05
Temperature plugs, °F.											
1†											
2	597	603	575	550	531	524	490	487	460	460	417
3	621	621	597	566	544	538	497	490	453	450	385
4	621	624	597	572	547	541	516	516	503	497	471
5	615	609	575	554	524	519	490	487	460	453	417
6†											
7	636	639	600	575	541	535	516	512	509	509	497
8†											
9	618	615	591	579	554	550	528	531	519	519	516
10	651	654	606	585	547	535	506	503	500	490	487
11	597	603	563	550	524	522	497	487	484	503	453
12	645	645	597	579	528	522	460	450	410	410	318
13	627	627	569	547	500	497	392	392	314	247	130
14	609	609	579	569	544	541	523	523	500	467	450
Av.	621	622	586	566	535	529	492	489	465	415	415
Max.	651	654	606	585	554	550	531	528	519	519	516
Min.	597	603	563	547	500	497	392	392	314	247	150

\* No water.

\*\* Water turned on after readings were taken.

† Out of order.

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## CONDUCTIVITY DATA OF AQUEOUS MIXTURES OF HYDROGEN PEROXIDE AND NITRIC ACID<sup>1</sup>

BY W. H. HATCHER<sup>2</sup> AND D. W. MACLAUCHLAN<sup>3</sup>

### Abstract

Solutions of hydrogen peroxide and nitric acid are unstable when the concentration of the latter is greater than 50%. The conductivities of nitric acid solutions of concentrations lower than this value in water and water-peroxide mixtures have been determined, and the results indicate the formation of one or more unstable peroxides or peracids apparently incapable of ionizing.

### Introduction

The present paper is an extension of the investigations of Maass and co-workers (1, 7, 8) and others (3, 5) on solutions of electrolytes in pure and in aqueous hydrogen peroxide. These have shown that inorganic salts in hydrogen peroxide as pure as 100% give conductivity curves closely resembling those obtained when pure water is used as the solvent; organic acids, on the other hand, show decreasing conductivity with increase of peroxide concentration, coincident with the formation of the so-called peracids. Also, the measured dielectric constants of hydrogen-peroxide-water mixtures, which show a maximum of 121 for 36.3% peroxide, provide no evidence that a high dielectric constant contributes directly to the ionizing power.

The following pages present the first study of the conductivity of a strong acid in hydrogen-peroxide-water mixtures.

### Preparation of Reagents

### Experimental

The hydrogen peroxide used throughout was prepared from 30% commercial material containing no inhibitor; this was distilled, concentrated, and, where necessary, crystallized; it contained no impurity other than water.

Nitric acid was prepared by the method of Manley and Velej (9), whose values for the conductivity of nitric acid are accepted as standard. In spite of the thoroughness of their method of preparation, it is felt that the values obtained by the dilution of highly concentrated nitric acid cannot be as trustworthy as those provided by the pure unconcentrated acid. Since the conductivities of the acid-water and acid-water-peroxide mixtures were

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measured by a uniform technique in order to find any differences that might exist between the two, such slight errors as might arise from the preparation of the acid tended to cancel out.

#### Mixing of the Reagents

Preliminary experiments in mixing hydrogen peroxide and nitric acid showed unexpected evidence of almost explosive violence at high concentrations, whereas quite dilute solutions gave no trace of decomposition even after days of standing. It was thus early evident that the range of concentrations to be measured is restricted.

In order, therefore, to determine the limiting concentrations of reagents suitable for sustained physical measurement, various mixtures of 30 cc. or less were made in clean Pyrex test tubes and small Erlenmeyer flasks, and their behavior was carefully studied. Three types of mixtures were soon found. The first type consisted of those in which the reagents on being poured together immediately bubbled violently and then gushed forth to a height of two or three feet, crackling violently when falling on metallic gauze and occasionally igniting the bench-tops. When this occurred, the odor of ozone was very strong, brown fumes were distinctly visible, and considerable heat was developed; these reactions are listed as "instantaneous", and such mixtures termed "reactive". The second type consisted of somewhat less concentrated solutions that took from a few seconds to several hours to react, and even in those that took several hours a climax was reached which could be predicted beforehand; an originally slow ebullition increased gradually with the temperature until the latter reached 40°, 70° or even 100° C., whereupon the evolution of brown fumes became rapid; after this climax the reaction subsided rapidly. The early part of these slow reactions is due to decomposition of hydrogen peroxide by the heat of mixing of the reagents, and the reaction is delayed by cooling or using an open beaker instead of a narrow test tube. When it was possible to trap the products of these reactions, the

residue represented most of the nitric acid employed but showed complete absence of any hydrogen peroxide. The third type was stable for a period of 24 hr., and is here termed "unreactive".

Fig. 1 shows a convenient representation of the limits of reactivity of these mixtures obtained by adding various volumes of nitric acid of different concentrations to 1 cc. of 62.9% hydrogen peroxide in water at 21 to 23°C. A large collection of data showed that the controlling factor in promoting reaction is

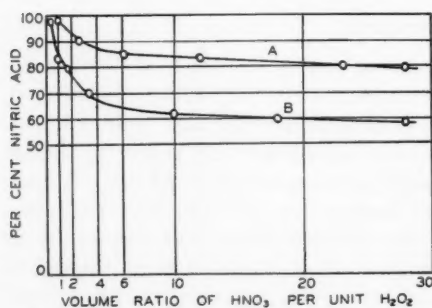


FIG. 1. Reacting volumes of nitric acid and hydrogen peroxide; showing volumes of aqueous nitric acid of various concentrations added to one volume of 62.9% hydrogen peroxide at 21 to 23° C. A, lower limit of instantaneous reaction; B, lower limit of any noticeable reaction.

the concentration of nitric acid rather than that of the peroxide, and that it is not possible to have a concentration of acid greater than 50% in the acid-hydrogen-peroxide-water mixture without the possibility of reaction.

Those mixtures which were "unreactive", e.g., below Curve B in Fig. 1, were made to react by heating, but even then only a mild decomposition with loss of oxygen occurred.

When the same type of container was used in the above-mentioned experiments, the results were easily reproducible; but the addition of pieces of capillary tubing largely increased the rate of decomposition, while mixing the reagents in beeswax-lined glass containers decreased it appreciably.

In order to avoid any possibility of decomposition during the measurements to be described, concentrations represented by points below Curve B, Fig. 1, were chosen, the temperature was kept from start to finish at 0° C. by means of an ice-water bath, and Pyrex containers were used throughout.

#### Determination of Conductivity

The method used for determining the conductivity was the static one, and the apparatus similar to that previously described (1, 3); all connecting wires were shielded in copper tubing, and the electrodes were thin sheets of gold, 4 by  $\frac{1}{4}$  in., since tin and platinum were found unsuitable in the presence of both nitric acid and hydrogen peroxide. Manley and Veley (9) and Jones and Murray (5) used the a-c. method of Kohlrausch for nitric acid-water mixtures, and although the authors obtained small differences using the static method, the accuracy of the latter method is attested by the excellent agreement with the standard values for oxalic acid.

Three cells of different diameter were used, and, standardized with potassium chloride, showed cell-constant values of 13.56, 108.03, and 579.6. A check on the procedure, molar oxalic acid being used, gave a specific conductivity at 18° C. of  $589.5 \times 10^{-4}$  as compared with the accepted value of  $590 \times 10^{-4}$ . In the preparation of each mixture, the solutions of nitric acid and hydrogen peroxide, whose concentrations were accurately known, were added to the exact quantity of water required (if any); these were accurately weighed in and the specific gravity of each mixture immediately determined. For convenience of treatment the experi-

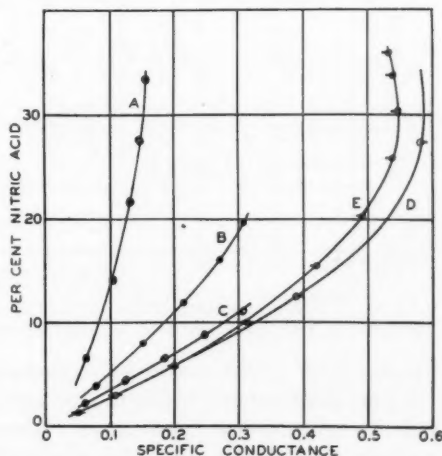


FIG. 2. Specific conductance of nitric acid in water and hydrogen peroxide. A, water = 22 to 25% by weight; B, water = 55 to 57%; C, water = 75 to 77%; Per cent  $H_2O_2 = 100 - (H_2O + HNO_3)$ ; D, nitric acid in water only (authors); E, same (Manley and Veley).

mental values obtained are shown in weight percentage unless otherwise stated.

In Fig. 2 are the curves showing the specific conductance of mixtures of nitric acid, hydrogen peroxide, and water. The discrepancy between *D* and *E* can be partly accounted for by the difficulty in obtaining pure nitric acid of high concentrations. Also the difficulty of measuring the conductivity of concentrated acids is evidenced by Newbery's value for sulphuric acid (12) which is 3% lower than that of Kohlrausch and Grotrian (6) and was substantiated by the work of Marie and Noyes (10). Incidentally Manley and Veley believed nitric acid to be a mixture of nitric acid, water, and nitrogen pentoxide.

In contrast to organic acids (3), nitric acid and hydrogen peroxide give an immediate reading which does not change with time, as shown by a mixture of 19.93% of nitric acid, 24.67% of hydrogen peroxide, and 55.40% of water whose specific conductance remained at 0.300 over a period of 24 hr.

At low concentrations of nitric acid and high concentrations of hydrogen peroxide, the effect of the latter on the conductance though small was taken into account by determining its specific conductance separately and subtracting it proportionately from the total value obtained from the mixture. These final values are those shown in Fig. 2.

Fig. 3 shows a different plotting of some of the results obtained, and Fig. 4 shows the molar conductivity of such solutions.

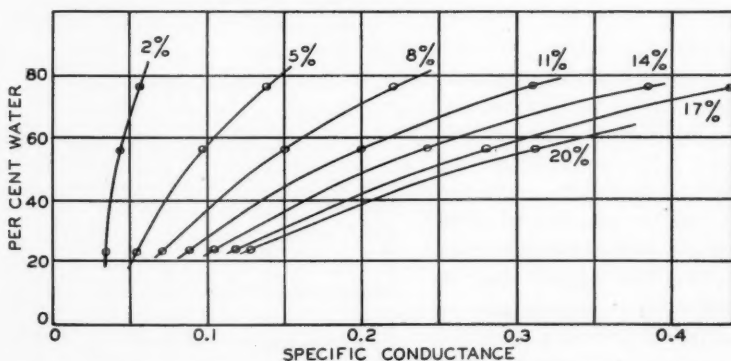


FIG. 3. Specific conductance of nitric acid in water-hydrogen-peroxide mixtures. Weight percentages of nitric acid and water as shown; percentage of peroxide =  $100 - (\text{H}_2\text{O} + \text{HNO}_3)$ .

#### *The Viscosity of Nitric-acid-hydrogen-peroxide-water Mixtures*

Equal volumes of 31% nitric acid and 34% hydrogen peroxide were mixed and the time of flow taken in an Ostwald viscosimeter 0° C.; the specific viscosity was found to be 1.093, whereas that of 31% nitric acid is 1.19 and that of 34% peroxide, 1.00.

#### *The Conductivity of Sulphuric Acid in Aqueous Hydrogen Peroxide*

Several determinations were made at 18° C. for comparison with the standard values, sulphuric acid, 41.7% and 87.7%, in water only, being

used: the respective specific conductances were 0.667 and 0.1076 as compared with 0.662 and 0.108 obtained by Kohlrausch and Grottrian (6). The specific conductance of 45% sulphuric acid in water at 18° C. is 0.620; the same concentration of acid with 3.34, 15.6, and 22.0% of hydrogen peroxide gave respective specific conductances of 0.536, 0.341, and 0.196.

#### *Chemical Tests of Nitric-acid-hydrogen-peroxide Mixtures*

Whereas neither hydrogen peroxide nor nitric acid shows any immediate reaction with benzene, a "reactive" mixture of the two, free from nitrous acid, produces a definite and persistent greenish-yellow coloration (11, p. 382). An "unreactive" mixture gave no such coloration but did produce iodine instantaneously on addition to a very dilute neutral solution of potassium iodide; with a more concentrated mixture—34% of peroxide and 31% of acid—a very large instantaneous precipitate of iodine was produced, though with no apparent liberation of oxygen even after several hours.

These tests, especially the latter, are considered satisfactory evidence of peracid formation.

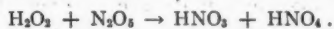
#### **Discussion of Results**

The instability of hydrogen-peroxide-nitric-acid-water mixtures is apparently due to the formation of a highly unstable complex, which, forming immediately on the mixing of the reagents and in proportion to their concentrations, decomposes exothermally; the accumulation of this heat hastens the decomposition so that in the vicinity of certain critical concentrations the evolution of oxygen and nitrogen oxides may occur with violence. This is, of course, in line with the instability of nitric acid itself of concentrations above 70%.

This unstable complex may be a peracid or a peroxide of nitrogen, for the previously noted observation of Manley and Veley that the formula  $HNO_3$  is an ideal expression to represent the presence of  $HNO_3$ ,  $H_2O$ , and  $N_2O_5$  all at once might be taken to suggest the existence of  $HNO_4$ ,  $HNO_5$ , etc., and also  $N_2O_6$ ,  $N_2O_7$ , etc. Shilov and co-workers (15) represent a reaction between nitrous acid and hydrogen peroxide as



Friend (2, p. 333) states that at low temperatures pure hydrogen peroxide and nitrogen pentoxide together show the characteristics of a peracid; thus



Raschig (14) on treating nitrous acid with 3% hydrogen peroxide solution concluded that pernitric acid is produced, which slowly decomposes into nitric acid and hydrogen peroxide:



Pollak (13) established the formation of pernitric acid from nitric acid and hydrogen peroxide in the presence of potassium bromide. Also Helbig (4) claimed the formation of an unstable  $N_2O_6$  when a series of electrical discharges

was sent through liquid air; this substance he reported as decomposing, sometimes explosively, with the evolution of brown fumes.

In the absence of any exact quantitative data regarding the composition of these peracids either from the literature or in the work so far of the present authors, even the term "pernitric acid" is held unjustifiable.

However, the results here presented, pure nitric acid—free from nitrous acid—and pure hydrogen peroxide being used, show that the behavior of this mixture is in accord with that of mixtures in which sulphuric and many organic acids were employed in producing an electrical conductivity lower than that obtained when the acid–water mixture alone is used.

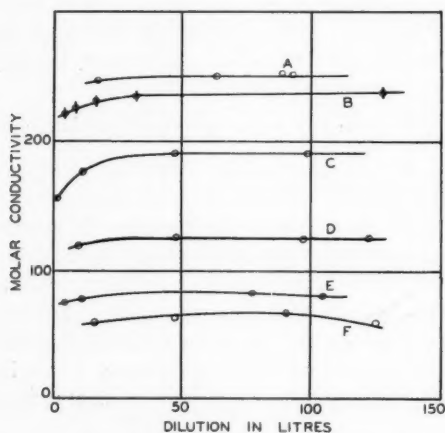


FIG. 4. Molar conductivity of nitric acid in water and hydrogen peroxide. A, in water only (authors); B, same (Jones and Murray); C, in water and hydrogen peroxide (19.2%); D, in water and hydrogen peroxide (40.0%); E, in water and hydrogen peroxide (61.4%); F, in water and hydrogen peroxide (79.6%).

conduct the current. This is also exemplified by the figures in Table I. Here a small change in nitric acid and dilution but a large increase in peroxide content produce a striking decrease in molar conductivity.

The apparent unimportance of viscosity and dielectric properties points to the possible union of nitric acid and hydrogen peroxide to form a non-conducting substance as the only explanation of the results here related. Indeed it is possible, all other factors being ignored, to show that at any fixed water-content of these mixtures the observed specific conductance differs from that of nitric acid in water only by an amount

Fig. 2 shows that at any concentration of nitric acid in a mixture of water and hydrogen peroxide the last named produces a decrease in the specific conductance approximately proportional to its concentration. This fact is better shown in Fig. 3 where extrapolation to zero water concentration indicates that solutions of pure nitric acid in pure hydrogen peroxide should give a specific conductance of approximately 0.04.

In Fig. 4 are shown the values for molar conductivity of nitric acid in water (the authors' and Jones') and in water–peroxide mixtures; thus the higher the peroxide content of the medium the less able is the solution to

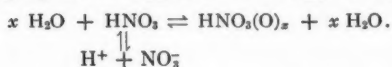
TABLE I

Nitric acid, %	Hydrogen peroxide, %	Dilution in litres	Molar conductivity
19.65	25.47	0.264	81.5
20.82	54.88	0.218	28.5

that is determined by the removal from the ionic state of molecules of nitric acid and hydrogen peroxide. Such an empirical relation, however unjustified, does suggest that the current carried is a measure of the "free" hydrogen ions in "free" water.

At any rate the values obtained definitely point to retention of the electrolyte by hydrogen peroxide apart from the possible influence of viscosity, dielectric properties, solvation of the ions by hydrogen peroxide, or changes in water aggregations.

The following equation suggests an analogy to organic peracids:—



Sulphuric acid shows the same tendency as nitric acid to decreased conductance; this is in accord with the work of Maass and Matheson (8). Jones and Murray (5) found that oxalic and sulphuric acids cause a freezing-point depression in dilute hydrogen peroxide solutions greater than that when pure water is used as the solvent, and the opposite of this for salt solutions; from this they argued that in mixtures of acids and hydrogen peroxide the dissociation is greater, and in mixtures of salts and hydrogen peroxide there is compound formation. The peroxide content was so small, however, that these explanations do not seem convincing.

The investigation of nitric-acid-peroxide mixtures is proceeding with a view to establishing the nature of the possible peracid or peroxide involved.

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# THE KINETICS OF THE DECOMPOSITION REACTIONS OF THE LOWER PARAFFINS

## II. ISOBUTANE<sup>1</sup>

By E. W. R. STEACIE<sup>2</sup> AND I. E. PUDDINGTON<sup>3</sup>

### Abstract

The kinetics of the thermal decomposition of isobutane has been investigated over an initial pressure range of from 5 to 60 cm., and at temperatures from 522 to 582° C. The initial first order rate constants at high pressures are given by

$$\log k = 13.92 - \frac{63500}{2.3 RT} \text{ sec.}^{-1}$$

The results are in general agreement with those obtained by previous investigators. The reaction rate falls off with diminishing pressure, and the first order rate constants in a given run diminish strongly as the reaction proceeds. This behavior is similar to that of *n*-butane.

Analyses of the products of the reaction were made at various stages, temperatures, and initial pressures by low-temperature distillation in a still of the Podbielniak type. The initial products were found by extrapolation to be H<sub>2</sub>, 35; CH<sub>4</sub>, 14; C<sub>2</sub>H<sub>6</sub>, 0.9; C<sub>3</sub>H<sub>8</sub>, 0.9; C<sub>4</sub>H<sub>10</sub>, 14; and C<sub>4</sub>H<sub>8</sub>, 35%. The results are compared with those of other workers.

### Introduction

In a recent paper from this laboratory (16) it was pointed out that the thermal decomposition reactions of the simple paraffin hydrocarbons offer interesting possibilities for a study of the effect of chemical configuration on the reaction rate. A review of the literature by one of us (14) has shown that the existing kinetic data are far too unreliable to enable any comparison between the various members of the paraffin series. This is particularly true of the isomers of butane. In view of this an investigation has been made of the decomposition of the two butanes. The present paper deals with that of isobutane.

Pease (10), and later Pease and Durgan (11), using a flow method, first showed that the reaction was first order and homogeneous. The velocity constant at 600° C. was found to be  $7.6 \times 10^{-3} \text{ sec.}^{-1}$ , and the activation energy was very roughly estimated to be 65,000 cal.

Paul and Marek (9), using a similar method, obtained a value of 66,000 cal. for the activation energy. Their velocity constants varied from  $2.8$  to  $32.6 \times 10^{-3} \text{ sec.}^{-1}$  at temperatures from 550° to 610° C. Their work was done at low conversions, about 5% of the isobutane being decomposed.

Frey and Hepp (5) worked at one temperature only, 575° C., and found a velocity constant of  $4.8 \times 10^{-3} \text{ sec.}^{-1}$ .

Marek and Neuhaus (8), Hurd and Spence (6), and others (4) examined the products of the reaction only. Their results will be discussed later.

<sup>1</sup> Manuscript received June 14, 1938.

Contribution from the Physical Chemistry Laboratory, McGill University, Montreal, Canada, with financial assistance from the National Research Council of Canada.

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<sup>3</sup> Graduate Student, Department of Chemistry, McGill University.

### Experimental

In this investigation a static system was used almost entirely, a flow apparatus being employed for a few runs to study the products at low conversions. As the static system and experimental technique have been described elsewhere (16), they will not be discussed here.

The flow system is shown diagrammatically in Fig. 1. Purified isobutane was stored as a liquid in a bulb connected to the apparatus by a ground joint. In series with the gas supply was a 10 litre volume which served to stabilize the pressure. Stopcocks, which had been scratched with a file, at *A* and *B*, served to control the flow of gas. The rate of flow of the gas could be estimated by turning the three-way stopcock so that the gas flowed directly into the manometer.

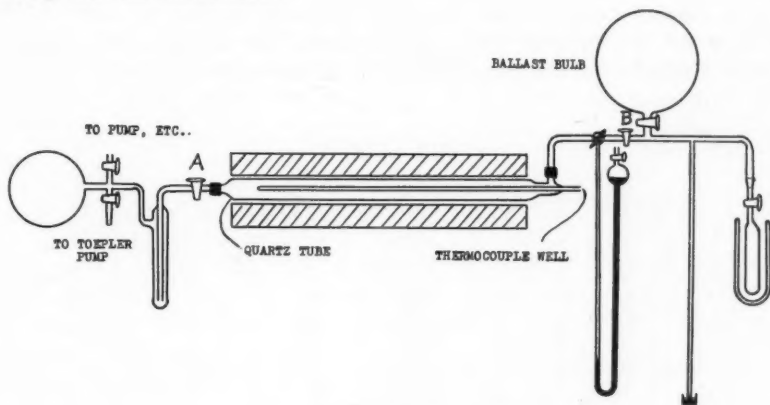


FIG. 1. Flow apparatus.

The reaction vessel for the flow system was a two-foot length of transparent quartz tubing having a volume of 80 cc. Into one end was sealed a thermocouple well which extended nearly the entire length of the vessel. Since the remainder of the apparatus was of soft glass, the reaction vessel was attached with de Khotinsky cement.

The furnace consisted of a piece of  $1\frac{1}{2}$  in. iron pipe wound with nichrome ribbon (0.44 ohm per ft.), and wrapped with asbestos paper. At the temperature of operation the reaction vessel had a temperature gradient of  $5^\circ$  from the centre to either end. The temperature of any location could be controlled to  $\pm 1^\circ$ .

A trap immersed in liquid air, in series with an expansion bulb of two litres volume, kept the back pressure sufficiently low that the rate of flow was not appreciably altered during a run. On completion of an experiment the products were expanded into the two litre bulb, pumped into a portable gas-holder by means of a Toepler pump, and transferred to the low-temperature distillation apparatus. The small capacity of the analytical still (about

one litre of gas) limited the usefulness of the flow system in studying the products at low conversions.

Isobutane of 99% purity, obtained in cylinders from the Ohio Chemical and Mfg. Co., was purified in a low temperature still of the Podbielniak type prior to use. The purified gas contained no detectable impurity.

### Results

After the first few runs the rates became completely reproducible. Somewhat more polymerization to higher compounds occurred than with *n*-butane, although the total amount of higher products formed per run was negligible. After about 10 runs in the packed reaction vessel, the quartz packing became covered with a thin layer of carbon.

Runs carried to completion showed a pressure increase of about 108%. The amount in excess of 100% was doubtless due to secondary reactions, since analytical results showed that 25% pressure increase corresponded to 25% decomposition.

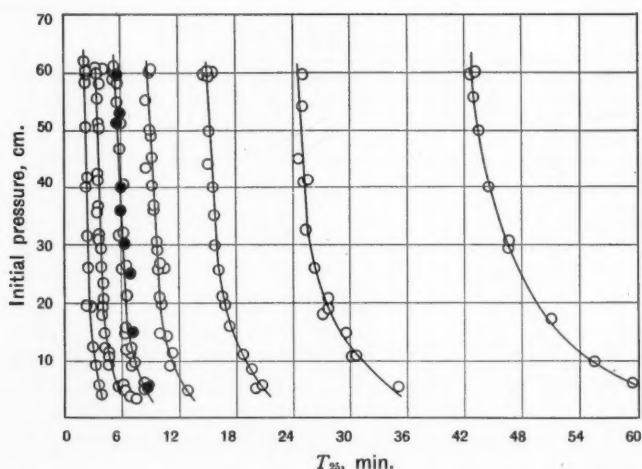


FIG. 2. Effect of pressure on rate. Curves from left to right are for temperatures 582, 572, 562, 552, 543, 533, 522, respectively. Full circles represent determinations with reaction bulb packed with crushed quartz.

Data for a typical run are given in Table I. Unimolecular constants are calculated on the assumption that 100% pressure increase corresponds to completion. Table II shows the effect of temperature and initial pressure on the rate of reaction. In the table,  $T_{12.5}$  and  $T_{25}$  correspond to pressure increases of 12.5 and 25% respectively.

The data of Table II are shown graphically in Fig. 2. It will be seen that the rate, as inferred from the times to fractional values, falls off with diminishing initial pressure. High pressure rates were obtained by plotting the

TABLE I  
DATA FOR A TYPICAL EXPERIMENT AT 562° C.  
Initial pressure, 41.90 cm.

Time, min.	P, cm.	k, sec. <sup>-1</sup>	Time, min.	P, cm.	k, sec. <sup>-1</sup>
0.5	2.00	$16.15 \times 10^{-4}$	39	29.75	$5.30 \times 10^{-4}$
1	3.35	13.81	46	31.85	5.18
3	6.95	11.50	56	34.18	5.05
5	9.52	8.62	71	36.75	4.92
8	12.65	7.50	84	38.32	4.88
12	16.08	6.73	113	40.90	5.04
15	18.28	6.40	138	42.30	—
22	22.56	5.87	243	45.00	—
31	26.85	5.51	278	45.60	—

fractional times against the reciprocal of the initial pressure and extrapolating to infinite pressure as shown in Fig. 3. Table III gives the values of the rate constants obtained in this way.

The theoretical value of the ratio  $T_{25}/T_{12.5}$ , 2.16, is considerably lower than the experimental values. This was also observed by us in the decomposition of *n*-butane, and has also been noted by Dinzes (1-3) in the decomposition of ethane and propane. Since the first order constants fall off rapidly in an individual run, as shown by Table I, this is, of course, to be expected.

As pointed out before (16), reaction rate curves must have identical forms at different temperatures if the calculated value of the activation energy is to be unaffected by the drift in the rate constants as the reaction progresses. The simplest way of testing this is to compare the values of the ratio  $T_{25}/T_{12.5}$  at various initial pressures and temperatures. Table IV gives data of this sort. As the value of this ratio is virtually independent of the initial pressure and temperature, the values in

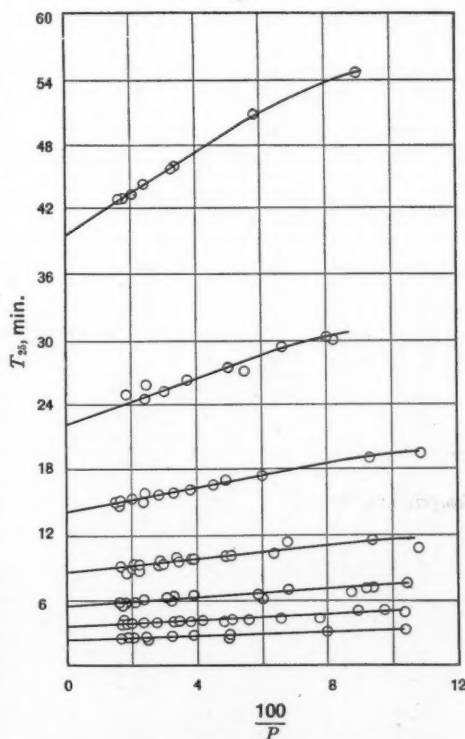


FIG. 3. Extrapolation of rates to infinite pressure. Curves from top to bottom are for temperatures 522, 533, 543, 552, 562, 572, 582, respectively.

TABLE II  
VARIATION OF REACTION RATE WITH TEMPERATURE AND PRESSURE

Initial pressure, cm.	$T_{12.5}$ min.	$T_{25}$ min.	Initial pressure, cm.	$T_{12.5}$ min.	$T_{25}$ min.
<i>Temperature, 522° C.</i>					
6.19	18.0	59.0	40.40	14.2	44.8
10.78	17.5	55.4	49.62	13.3	43.3
17.40	16.0	51.0	56.40	14.0	42.8
29.50	15.0	46.5	60.20	13.2	43.0
30.40	14.8	46.5	60.25	13.3	43.2
<i>Temperature, 533° C.</i>					
6.32	11.3	35.0	26.67	8.1	25.9
10.45	10.7	30.3	32.86	7.8	24.8
12.01	9.3	30.0	40.80	8.0	24.8
15.10	9.3	29.7	40.80	8.5	25.4
18.13	8.8	27.0	45.40	7.3	24.1
19.45	9.5	27.4	54.40	7.8	24.8
20.20	8.9	27.8	60.10	7.9	24.9
<i>Temperature, 543° C.</i>					
5.02	6.7	19.9	35.6	5.0	15.5
5.18	8.2	20.9	40.9	5.5	15.8
8.40	6.5	19.5	42.6	4.6	15.0
10.76	6.3	19.2	49.7	5.1	15.3
16.65	5.8	17.1	49.9	4.9	15.1
20.30	5.5	16.8	59.1	5.1	15.2
21.3	5.3	16.6	60.1	4.9	14.7
27.0	5.7	16.3	60.3	4.9	15.0
30.2	5.4	15.3	60.9	4.8	15.0
<i>Temperature, 552° C.</i>					
4.50	4.5	13.0	29.8	3.4	9.9
9.30	3.2	10.8	30.1	3.3	9.8
10.58	4.2	11.8	35.2	3.2	9.7
10.60	4.2	12.8	35.8	3.3	9.4
14.75	3.8	11.8	40.3	3.0	9.1
15.65	3.6	10.1	43.9	2.9	8.9
20.30	3.3	10.2	45.2	3.1	9.3
20.4	3.5	10.0	49.7	3.2	9.4
25.3	3.6	10.1	50.5	3.1	9.0
25.5	3.4	10.0	55.3	2.9	8.5
25.5	3.3	10.1	60.0	2.9	9.1
			60.2	3.1	9.1

TABLE II—*Concluded*  
VARIATION OF REACTION RATE WITH TEMPERATURE AND PRESSURE

Initial pressure, cm.	$T_{12.5}$ min.	$T_{25}$ min.	Initial pressure, cm.	$T_{12.5}$ min.	$T_{25}$ min.
<i>Temperature, 562° C.</i>					
4.85	2.6	8.3	25.9	2.1	6.3
5.22	2.7	8.3	30.8	2.1	6.3
5.36	2.9	8.5	31.5	2.1	6.0
6.65	2.8	8.0	40.3	2.1	6.2
8.65	2.1	6.3	47.6	2.1	5.9
9.80	2.5	7.5	51.2	2.0	6.0
10.61	2.5	7.3	55.0	1.9	5.6
10.81	2.2	7.2	59.6	2.0	5.9
11.42	2.6	6.8	59.7	1.9	5.6
14.95	2.2	6.9	60.0	1.9	5.8
16.50	2.2	6.2	60.0	1.9	5.8
20.40	2.2	6.8	60.0	1.9	5.7
25.2	2.1	6.4			
<i>Temperature, 562° C. Packed reaction vessel.</i>					
5.01	3.1	8.8	36.9	2.0	6.1
15.2	2.6	7.6	40.0	2.1	6.3
26.0	2.4	6.6	51.2	2.0	6.0
30.0	2.0	6.1	53.6	2.1	6.1
			59.8	1.9	5.9
<i>Temperature, 572° C.</i>					
3.0	2.8	7.0	30.3	1.4	4.0
4.3	2.2	6.1	30.8	1.3	4.0
5.3	2.1	6.1	35.8	1.3	3.7
5.5	2.3	6.3	36.2	1.3	3.9
5.5	2.0	5.4	41.0	1.3	3.8
9.6	1.7	4.9	42.4	1.4	3.8
11.2	1.7	5.0	50.7	1.3	3.9
12.8	1.5	4.3	51.3	—	3.8
15.1	1.5	4.4	55.3	1.3	3.9
18.0	1.3	3.9	58.3	1.3	3.9
19.8	1.4	4.2	60.0	1.3	3.8
20.7	1.4	4.1	60.4	1.3	4.0
23.3	1.4	4.1	60.7	1.3	3.9
26.3	1.3	4.0			
<i>Temperature, 582° C.</i>					
4.1	1.1	3.6	40.2	1.0	2.4
5.1	1.4	4.0	40.8	0.9	2.7
9.6	1.1	3.2	58.2	0.7	2.2
12.4	1.1	3.2	60.0	—	2.5
19.8	0.9	2.5	60.0	0.8	2.5
19.9	1.0	2.9	61.0	0.8	2.5
25.7	1.0	2.8	61.0	0.7	2.2
31.4	1.0	2.8	62.0	0.8	2.2

TABLE III  
 EXTRAPOLATION OF RATE DATA TO INFINITE PRESSURE

Temperature, °C.	$T_{12.5}$ , sec.	$T_{25}$ , sec.	$T_{25}/T_{12.5}$	$k \times 10^4$ , sec. <sup>-1</sup> (calculated from $T_{25}$ )
522	747	2382	3.15	1.21
533	408	1278	3.13	2.25
543	270	843	3.12	3.41
552	168	495	2.95	5.81
562	113	333	2.95	8.64
572	70	215	3.09	13.4
582	46	141	3.05	20.4

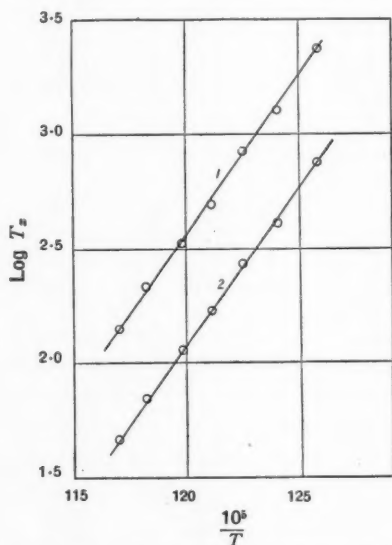


FIG. 4. The temperature coefficient of the reaction. Curve 1,  $\log T_{25} - \frac{10^5}{T}$ . Curve 2,  $\log T_{12.5} - \frac{10^5}{T}$ .

this we have for the initial high pressure rate

$$\log_{10} k = 13.92 - \frac{63500}{2.3 RT} \text{ sec.}^{-1}$$

That the reaction is not appreciably heterogeneous is shown by the position of the full circles in Fig. 3. These points represent runs in which the reaction vessel was packed with broken silica tubing, thereby increasing the surface/volume ratio by a factor of about 15 over that of the empty vessel in which the rest of the experiments were made.

Table III can be used to determine the energy of activation. This has been done graphically in Fig. 4, where Curve 1 is constructed from the values of  $T_{25}$  and Curve 2 from those of  $T_{12.5}$ . Identical values of 63,500 calories per mole are obtained for the energy of activation in each case. Whence we obtain for the velocity constants, calculated from the values of  $T_{25}$ , the equation

$$\log_{10} k = 13.62 - \frac{63500}{2.3 RT} \text{ sec.}^{-1}$$

Since the value of the velocity constant diminishes as the reaction proceeds, as shown by Table I, it is obvious that the above equation does not give the *initial* rate of reaction. From the data of a large number of runs, it appears that the initial rate constant is almost exactly 100% higher than that at  $T_{25}$ . Correcting for

### The Products of the Reaction

The products of the reaction were analyzed by low temperature fractional distillation. Samples for this purpose were taken at  $T_{12.5}$ ,  $T_{25}$ , and  $T_{50}$  at an initial pressure of 60 cm. over the entire temperature range. One analysis was also made from an experiment with an initial pressure of 20 cm. These results are given in Table V. Results of two runs made in the flow system at decompositions of 5.3 and 7.5% are given in Table VI. The mean values of all these results indicate that  $T_{50}$ ,  $T_{25}$ , and  $T_{12.5}$  as inferred from the pressure change really correspond to 51.0, 25.0, and 12.0% reaction respectively.

In the analyses, hydrogen and methane were distilled off together, and this fraction analyzed by combustion. It is perhaps worth pointing out that isobutene is difficult to determine accurately since its boiling point is below and close to that of isobutane, which is pres-

TABLE IV  
VALUES OF  $T_{25}/T_{12.5}$  AT VARIOUS TEMPERATURES AND  
PRESSURES

Temperature, ° C.	$T_{18}/T_{12.5}$			
	Infinite pressure	50 cm.	25 cm.	20 cm.
582	3.05	2.99	3.11	2.90
572	3.09	3.00	2.99	3.03
562	2.95	3.02	3.08	3.14
552	2.95	2.99	3.05	3.12
543	3.12	3.09	2.98	3.05
533	3.13	3.17	3.08	3.14
522	3.15	3.16	3.20	3.20

TABLE V  
THE PRODUCTS OF THE REACTION IN THE STATIC SYSTEM

[illegible]

ent in large amount, and, unless care is taken, normal butane, which is often present as an impurity in isobutane, may easily be included with it.

TABLE VI  
THE PRODUCTS OF THE REACTION IN THE  
FLOW SYSTEM

Initial pressure = 60 cm.  
Temperature = 572° C.

Products	Mole %	
H <sub>2</sub>	33.7	30.5
CH <sub>4</sub>	15.1	16.0
C <sub>2</sub> H <sub>4</sub>	—	1.5
C <sub>2</sub> H <sub>6</sub>	—	1.5
C <sub>3</sub> H <sub>6</sub>	16.3	21.0
C <sub>4</sub> H <sub>10</sub>	34.8	30.0
% C <sub>4</sub> H <sub>10</sub> decomposed	7.5	5.3

Small amounts of propane, of the order of 1% or less, were detected, but since an accurate separation of this small quantity from propylene is very difficult, it was included in the propylene fraction. It does not appear to be an initial product, and is probably formed by the hydrogenation of propylene.

From Table V it appears that the products are virtually independent of initial pressure and of temperature over the range examined.

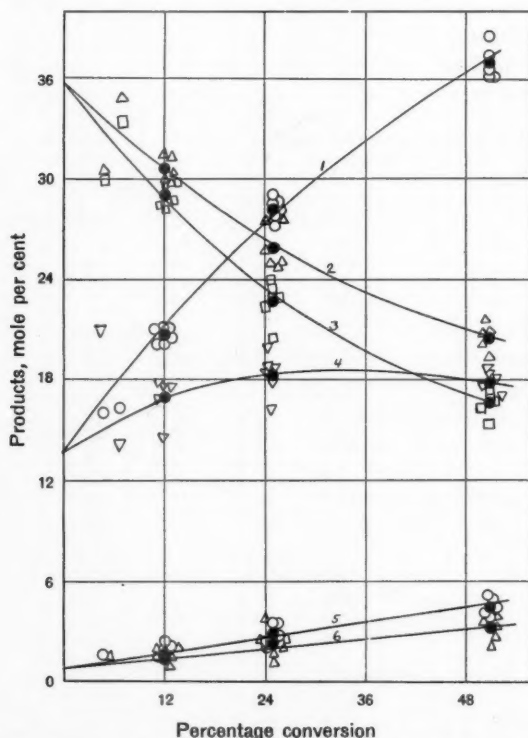


FIG. 5. Extrapolation to initial products. Curve 1, methane; Curve 2, hydrogen; Curve 3, butylene; Curve 4, propylene; Curve 5, ethane; Curve 6, ethylene. Filled circle in each case is the mean of the group.

Initial products were obtained graphically, as shown in Fig. 5. The extrapolated values thus obtained are:— $\text{H}_2$ , 35.0;  $\text{CH}_4$ , 14.0;  $\text{C}_2\text{H}_4$ , 0.9;  $\text{C}_2\text{H}_6$ , 0.9;  $\text{C}_3\text{H}_6$ , 14.0;  $\text{C}_4\text{H}_8$ , 35.0 mole per cent.

### The Rate of the Reaction

### Discussion

Comparing the values of  $E$  and  $A$  with those of other workers, we have—

	$E$ , Kcal.	$\log_{10} A$	$K_{575}$ , $\text{sec}^{-1}$
Pease and Durgan	65.0	14.23*	$1.6 \times 10^{-3}$
Paul and Marek	66.0	14.89	$7.1 \times 10^{-3}$
Frey and Hepp	—	—	$4.8 \times 10^{-3}$
This investigation	63.5	13.92	$3.0 \times 10^{-3}$

\*Calculated from the value given for 600° C.

A similar comparison for  $n$ -butane follows—

Frey and Hepp	61.4	13.53	$4.8 \times 10^{-3}$
Paul and Marek	73.9	17.05	$9.8 \times 10^{-3}$
Steacie and Puddington	58.7	12.71	$3.7 \times 10^{-3}$

In both cases the agreement of our data with those of Frey and Hepp is satisfactory. Agreement with the results of Paul and Marek is considerably better with isobutane than with  $n$ -butane. From our work it appears that while the activation energy for isobutane is somewhat higher than that for  $n$ -butane, the large difference between the two reported by Paul and Marek is fictitious.

In our paper on the decomposition of  $n$ -butane it was pointed out that the calculated value of the activation energy was somewhat higher at low pressures than at high, owing to the slight variation with temperature of the falling off in rate with pressure. From our data the difference between the true activation energy and that calculated from rates at atmospheric pressure was determined, and applied as a correction to the results obtained by other workers at atmospheric pressure. Owing to an arithmetical error, this calculated correction was too high. The proper correction is 1.7 Kcal. instead of 7.5 as given. Correcting the data for  $n$ -butane in this way, we obtain

Frey and Hepp	59.7 Kcal.
Paul and Marek	72.2
Steacie and Puddington	58.7

In other words there is now almost exact agreement with the results of Frey and Hepp.

If the same type of calculation is made for isobutane, we have

True activation energy	63.5 Kcal.
Calculated from results at	
76 cm.	63.5
33 cm.	63.6
20 cm.	64.0

In this particular case, therefore, there is no correction to be applied to results obtained at atmospheric pressure.

#### *The Products of the Reaction*

A comparison of the products obtained by various workers is given in Table VII. Fair agreement exists throughout, provided that the products are compared at the same degree of decomposition. The work of Frey and Hepp was done within the temperature range of this investigation, while that of Marek and Neuhaus, and Hurd and Spence was done at a slightly higher temperature (600°C.).

Qualitative agreement with the predictions of the Rice free radical theory (13) is obtained, since the chief products are  $H_2$ ,  $C_4H_8$ ,  $C_3H_6$ , and  $CH_4$  as predicted. However, on the Rice theory the ratio

$$\frac{C_4H_8 + H_2}{CH_4 + C_3H_6}$$

should be equal to 1.1. Actually, the experimental value of this ratio is 2.5. Whether or not the compound decomposes by a free radical mechanism seems to be an open question at the moment. It may, however, be remarked that the value of the activation energy obtained in this work is not very much above the activation energy of the split into free radicals (12, 13), and hence it is not necessary to postulate long chains if a free radical mechanism is to hold. The falling-off in rate with diminished pressure,

TABLE VII  
COMPARISON OF THE PRODUCTS OBTAINED BY VARIOUS WORKERS

Observers	Percent $C_4H_{10}$ decomposed	$H_2$	$CH_4$	$C_2H_4$	$C_2H_6$	$C_3H_6$	$C_3H_8$	$C_4H_8$
Marek and Neuhaus	0.0	31.5	17.5	—	1.2	17.0	—	31.5
Steacie and Puddington	0.0	35.0	14.0	0.9	0.9	14.0	—	35.0
Frey and Hepp	17.4	24.4	21.9	1.1	1.2	16.2	5.0	30.0
Steacie and Puddington	17.4	27.6	25.4	1.8	2.2	17.8	—	25.4
Frey and Hepp	6.7	29.5	20.6	0.0	1.1	15.7	1.9	31.1
Steacie and Puddington	6.7	30.8	18.6	1.2	1.4	15.9	—	32.2
Hurd and Spence	22.0	21.3	35.5	3.5	—	17.3	—	22.5
Steacie and Puddington	22.0	26.8	26.4	2.0	2.5	18.0	—	23.9

discussed in the next section, furnishes some evidence in favor of a free radical mechanism. Furthermore, as shown by Table I, the velocity constants fall off very strongly in an individual run. In the later stages of the reaction this is partly due to the back hydrogenation reactions coming into play. In the early stages of the reaction, however, the falling-off is even more pronounced, and calculation from the equilibrium constant of the dehydrogenation reaction (4) shows that at this stage the back reaction is negligible. The effect may therefore be due to some sort of chain process.

*The Effect of Pressure on the Rate of Reaction*

As was the case with the normal isomer, the rate of decomposition of isobutane falls off strongly with decreased initial pressure. This effect is rather surprising for such complex molecules. If we apply the Kassel theory (7), and put the number of oscillators equal to  $(3n - 6)$ , where  $n$  is the number of atoms in the molecule, we obtain  $s = 36$ . Subtracting the number of C-H bonds, as usual, since the C-H valence vibrations are unlikely to be thermally excited at these temperatures, we get  $s = 26$ . With this value of  $s$ , and any reasonable assumed frequency, the theory predicts no falling-off in rate until very low pressures are reached. To get agreement with experiment it is necessary to assign to the parameters the following values:

$$\begin{aligned}s &= 10 \\ \sigma &= 4 \times 10^{-8} \text{ cm.} \\ m &= 22 \\ \nu &= 1000 \text{ cm.}^{-1}\end{aligned}$$

Fig. 6 shows the agreement with experiment under these circumstances, the solid line representing the theoretical curve, and the circles the experimental points at 562° C.

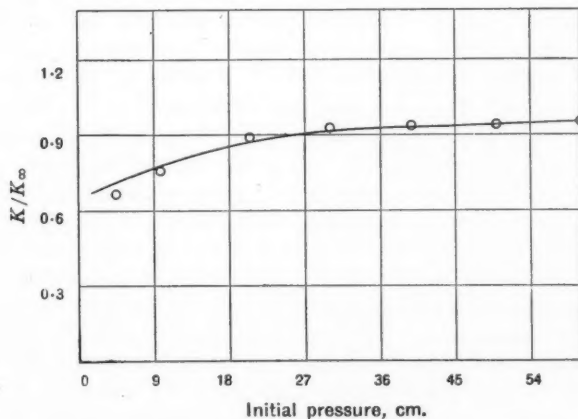


FIG. 6. Application of Kassel equation. Solid line represents falling-off as calculated from Kassel theory. Circles represent experimental values.

Since the isobutane molecule contains only C-C and C-H bonds, it appears unlikely that energy transmission from one part of the molecule to another should be difficult and result in the "freezing out" of some of the vibrational degrees of freedom. The effect is therefore, perhaps, to be ascribed to some complexity in the reaction such as the participation of free radicals. It is hoped that work now in progress (15) may throw further light on this point.

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## MEASUREMENT OF THE DIELECTRIC CONSTANT OF CELLULOSE<sup>1</sup>

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### Abstract

A method has been devised for the measurement of the dielectric constant of a material that cannot be made to completely fill a condenser. The following is the procedure adopted: Two completely miscible liquids are so chosen that the dielectric constant of the material under examination lies between the two values for the liquids. The dielectric constants of solutions of *A* and *B* ranging from 100% *A* to 100% *B* are measured. A curve is drawn showing the relation between dielectric constant and percentage composition. The condenser used is then partly filled with the fibrous material. The solutions of *A* and *B* are introduced into the condenser and the net dielectric constants are determined. A second curve is drawn showing this relation. The point of intersection of the two curves gives the composition of that liquid that has the same dielectric constant as the fibrous material.

This method has been applied to the measurement of the dielectric constant of cellulose, benzene and ethylene dichloride being used. A value of 6.1 has been obtained for this constant.

### Introduction

In an effort to obtain a clearer insight in regard to the cellulose-water system, Argue and Maass (2) resorted to a measurement of the dielectric constant of the water adsorbed on cellulose. A more precise interpretation of their results was prevented at that time, however, by the lack of a value for the dielectric constant of standard cellulose. The present investigation was undertaken for the purpose of establishing such a value.

The most widely used method for the measurement of the dielectric constant is based upon the relation that defines the dielectric constant of a material as numerically equal to the ratio of the capacity of a condenser when filled with the material to the capacity of the same condenser when empty. Some difficulty is encountered in attempting to apply this method to substances (such as fibrous materials) which cannot be made to completely fill the condenser space. Argue and Maass (2) have shown on theoretical grounds that the capacity of a condenser partly filled with a given weight of a fibrous material depends on the orientation of the fibres with respect to the condenser plates. If the fibres could be made to assume a regular arrangement such as parallel or at right angles to the plates, then by using the formulas developed by the above workers it would be possible to calculate the dielectric constant of the material from a measurement of the capacity of the partly filled condenser. If, however, the fibres possess a random distribution within the condenser space, as in the case of cellulose, the above-mentioned method cannot be used.

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A method has been devised for the measurement of the dielectric constant of fibrous materials having as its basis the following considerations. Consider a condenser filled with a given liquid. Let us now replace some of the liquid in the condenser space by an equal volume of fibrous material. If the dielectric constant of the latter is the same as that of the liquid, the capacity of the condenser will undergo no change and will be independent of the particular manner of distribution of the fibrous material in the condenser space. This can be proved mathematically by substitution in the formulas of Argue and Maass (2) which are given below.

$$\epsilon' = \frac{C'}{C} = \frac{1}{\frac{V_l}{V\epsilon_l} + \frac{V_f}{V\epsilon_f}} \quad (1)$$

$$\epsilon'' = \frac{C''}{C} = \frac{V_l\epsilon_l}{V} + \frac{V_f\epsilon_f}{V} \quad (2)$$

Equation (1) represents the net dielectric constant,  $\epsilon'$ , when the condenser, which has a capacity  $C$  when filled with a fluid of unit dielectric constant, is filled with a liquid of dielectric constant  $\epsilon_l$  and fibrous material of dielectric constant  $\epsilon_f$  with the *fibres parallel to the plates*.  $V_l$  is the volume of liquid and  $V_f$  that of the fibrous material; therefore  $V_l + V_f = V$ .

Equation (2) represents the net dielectric constant  $\epsilon''$  when the fibres are *perpendicular to the plates*.

$C'$  and  $C''$  are the condenser capacities in the two cases.

If  $\epsilon_l = \epsilon_f = \epsilon$ , Equations (1) and (2) both take the form  $\epsilon' = \epsilon = \epsilon''$ .

In other words, the dielectric constant of the compound dielectric is independent of the particular distribution of the fibres relative to the condenser plates. Inasmuch as Equations (1) and (2) represent the extreme cases of fibre distribution, that is, parallel to the plates and at right angles, the same relation holds for any intermediate manner of distribution.

The above discussion indicates that the dielectric constant of a fibrous material can be measured provided that the condenser space unoccupied by the fibres is filled with a liquid having the same dielectric constant. Such a liquid is obtained in the following manner. Two completely miscible liquids,  $A$  and  $B$ , are so chosen that the dielectric constant of the material under examination lies somewhere between the two values for the liquids. The dielectric constants of solutions ranging from 100%  $A$  to 100%  $B$  are measured. A curve showing the relation between dielectric constant and percentage composition is drawn. The condenser used in the above-described measurements is then partly filled with the fibrous material. The solutions of  $A$  and  $B$  are introduced into the condenser and the resultant dielectric constants determined. A curve similar to the first one is drawn. The point of intersection of the two curves gives the composition and the dielectric constant of the liquid that has the same dielectric constant as the fibrous material. In this manner the dielectric constant of the fibrous material can be determined.

### Experimental

#### *Apparatus for Capacity Measurement*

The heterodyne method of capacity measurement was employed. The apparatus was originally described by Smyth (8), but it has been considerably modified by other workers in this laboratory as well as by the present authors. It consists essentially of two high-frequency oscillators of the vacuum tube type and a detector-amplifier unit (Fig. 1).

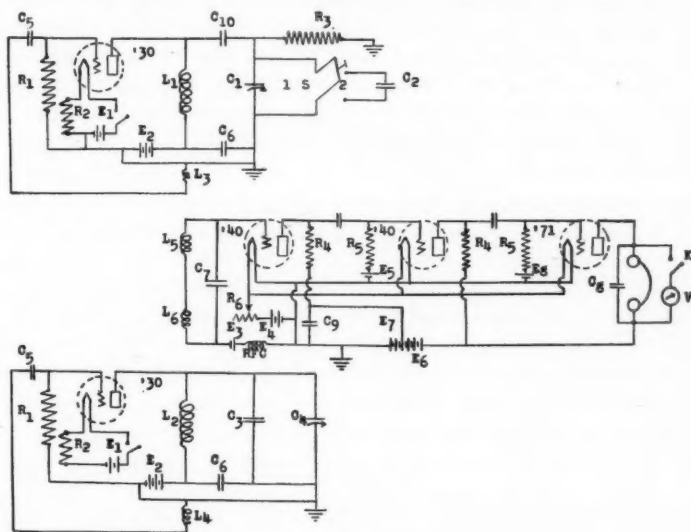


FIG. 1. Wiring diagram for measurement of capacity.

$R_1 = 50,000$ ohms.	$E_1 = 3$ volts.	$C_1 = 500$ $\mu$ f.
$R_2 = 15$ ohms.	$E_2 = 90$ volts.	$C_2 =$ Cell.
$R_3 = 12,500$ ohms.	$E_3 = 1.5$ volts.	$C_3 = 500$ $\mu$ f.
$R_4 = 0.25$ megohms.	$E_4 = 6$ volts.	$C_4 = 1,200$ $\mu$ f.
$R_5 = 5$ megohms.	$E_5 = 3$ volts.	$C_5 = 0.001$ $\mu$ f.
$R_6 = 6$ ohms.	$E_6 = 135$ volts.	$C_6 = 0.01$ $\mu$ f.
	$E_7 = 45$ volts.	$C_7 = 0.00025$ $\mu$ f.
	$E_8 = 27$ volts.	$C_8 = 0.002$ $\mu$ f.
		$C_9 = 2$ $\mu$ f.
		$C_{10} = 0.1$ $\mu$ f.

The two oscillator circuits are shown respectively at the top and bottom of Fig. 1. The inductances  $L_1$  and  $L_2$  consisted of 70 turns of No. 14 insulated copper wire wound on a form  $3\frac{3}{4}$  in. in diameter.  $L_3$  and  $L_4$ , consisting of 35 turns, were wound over  $L_1$  and  $L_2$  respectively. The capacitance  $C_1$  was a precision condenser of 500  $\mu$ f. (General Radio, Type 247 E).  $C_2$  was the experimental condenser containing the substance whose dielectric constant was to be measured.  $C_3$  was approximately equal to  $C_1$  in capacity.  $C_4$  (about 1200  $\mu$ f.) was necessary to offset the capacity of the long leads used in conjunction with  $C_1$  and  $C_2$ . A one plate vernier condenser attached to  $C_4$  afforded a fine adjustment.

Several precautions were taken to ensure frequency stability of the oscillators. A heavy bus bar was used in wiring to avoid the capacity changes that result from the vibration of lighter wire. In order to obtain a more constant "A" voltage source, four batteries were connected in series-parallel since such an arrangement minimizes the current drain from each cell. A fixed resistor, rather than a rheostat, was used to drop this voltage to two volts. Heavy duty "B" batteries served to supply the plate voltages of the vacuum tubes. For purposes of shielding, each oscillator was housed in a sheet metal box, which was grounded. The variable condensers were included in the oscillator circuits in such a manner that the shafts, which extended beyond the metal shielding, were also grounded. The long leads, used in connecting the standard condenser and the experimental condenser to the oscillator, were shielded by placing the individual wires in copper tubing and grounding the latter.

In order to increase the accuracy with which the standard condenser could be read, it was placed in the centre of a circular wooden platform 5 ft. in diameter. A small mirror attached to the rotor shaft reflected a line image on to a millimetre scale fastened to the circumference of the platform. With this arrangement, readings could be estimated to within 0.1 mm. In order to avoid body capacity, a pulley arrangement was used so that the rotor could be turned from the edge of the platform. A vernier dial used in conjunction with the pulley system made possible a fine adjustment.

The oscillators were loosely coupled to the detector-amplifier unit (shown centrally in Fig. 1) by means of  $L_5$  and  $L_6$  each of which consisted of four turns of No. 22 wire on a bakelite form  $2\frac{1}{2}$  in. in diameter. (By increasing the number of turns on these coils, the intensity of the beat note can be increased. The above-mentioned number of turns, however, was sufficient.)  $L_5$  and  $L_6$  were placed in the metal boxes containing the oscillators, adjacent to  $L_1$  and  $L_2$  respectively.

The detector-amplifier unit was the same as that described by Smyth (8), with the following major exception. The output stage was operated in addition as a vacuum-tube voltmeter so that a visual indication of the null point could be obtained. (This depends on so choosing the bias of the tube that it operates on the non-linear part of its grid-voltage-plate-current curve.) The above unit also was shielded by means of a sheet metal box.

Before an attempt is made to locate the null point in this set-up, the reading on the voltmeter  $V$  (the three volt range of a Weston voltmeter Model No. 290) is first adjusted to a suitable value by means of  $R_6$ . The region of zero beat is determined by using the loud-speaker. The voltmeter, however, furnishes a more convenient and more sensitive means of obtaining the exact null point. As zero beat is approached, the reading given by  $V$  gradually increases. Just before the null point is reached, the voltmeter needle begins to oscillate. The more nearly the zero beat conditions are approached, the wider is the amplitude of the oscillating needle. As the exact null point is reached, however, the needle suddenly ceases its motion. The null point

extended over a slight "dead space", which was equal to approximately 0.1 cm. on the scale. With this method the dead space was much smaller than it was when the loud-speaker alone or even a pair of earphones was used. To minimize the effect of the dead space, the same side was always taken as the null point; that is, zero beat was always approached from the same direction.

The capacity was determined as follows. Switch  $S$  is left in Position 1 and the standard condenser,  $C_1$ , is set to read zero on the scale.  $C_4$  is then rotated until zero beat conditions obtain. Switch  $S$  is next placed in Position 2 and the standard condenser is rotated until zero beat conditions are again established. The difference between the two readings gives a measure of the capacity of  $C_2$ .

When the apparatus was first assembled, instead of a single null point, a series of zero beats was obtained; this indicated that the oscillators were beating against the carriers of broadcasting stations. It was found that the long leads to the standard condenser, even though shielded, were acting as antennas. When these were removed from the circuit, only one null point was obtained. The interfering signals were subsequently filtered out by means of  $R_3$  and  $C_{10}$ . The value of the blocking condenser is not critical, but it should be large enough to offer but slight impedance to a current of the frequency of the oscillator. The value of  $R_3$  was found to be quite critical, as values less than 10,000 ohms killed oscillation, while values greater than 15,000 ohms did not remove the interfering signals. No such filter circuit was necessary for the fixed oscillator as it did not include any long leads.

#### *Calibration of the Standard Condenser*

In later calculations the assumption is made that a straight line relation exists between the capacity of the standard condenser at a given setting and the corresponding scale reading. Linton and Maass (6) have shown that this is not strictly true. Accordingly, it is necessary to correct for the aberration from linearity in the above-mentioned relation. The following method was devised for calibrating the standard condenser. A small condenser was used to replace  $C_2$  in the variable oscillator, and the displacement of the null point produced by it over successive parts of the scale was determined. The lowest value was arbitrarily chosen as the unit value, and the differences between this and the remaining readings were calculated. A curve showing the relation between reading of the standard condenser and correction was then drawn. The accuracy of this method of calibrating the condenser was investigated by measuring the capacity of a given condenser over various parts of the scale. All the corrected values were found to agree much more closely among themselves than did the uncorrected ones.

#### *The Calculation of the Dielectric Constant*

The dielectric constant, as previously mentioned, is given by the ratio  $C'/C$ , where  $C'$  is the capacity of the condenser filled with the material and  $C$  is the capacity of the condenser empty. The capacity measurements taken under experimental conditions, however, include the capacity of the leads

which connect the unknown capacity to the measuring equipment. It is therefore necessary to allow for these.

We may write:

- (i) for the condenser when empty:  $L + C = kd_1$
- (ii) for the condenser when filled:  $L + C' = kd_2$
- (iii) for the leads:  $L = kd_3$

Where  $L$  is the lead capacity,

$C$  is the capacity of the condenser when empty,

$C'$  is the capacity of the condenser when filled,

$d_1$  is the scale reading for the empty condenser plus the leads,

$d_2$  is the scale reading for the filled condenser plus the leads,

$d_3$  is the scale reading for the leads,

$k$  is the proportionality factor connecting scale reading and capacity.

The dielectric constant  $\epsilon$  will be given in terms of scale readings by the relation:

$$\epsilon = \frac{kd_2 - kd_3}{kd_1 - kd_3}$$

$$\epsilon = \frac{d_2 - d_3}{d_1 - d_3} \quad (4)$$

Since the proportionality factor  $k$  does not appear in the final expression, we are not concerned with its value. Capacity measurements have been accordingly expressed in this work in terms of the scale readings of the standard condenser.

#### *Preparation of the Liquids*

#### **Experimental**

As there was considerable doubt concerning the value of the dielectric constant of cellulose, it was necessary to choose two liquids whose dielectric constants were somewhat far apart. It was also necessary to choose liquids that would not be adsorbed by the cellulose. The hydrocarbons, which are ideally suitable because they are not appreciably adsorbed, all possess low dielectric constants. It was one of these, benzene (dielectric constant, 2.27) that was chosen for the liquid of lower dielectric constant. There are, however, very few liquids that are not likely to be adsorbed that possess a high dielectric constant. Such compounds as those containing oxygen, hydroxyl groups, nitrogen, and unsaturated carbon, which are those that exhibit high dielectric constants, are also those that are most likely to be strongly adsorbed. It was decided to use ethylene dichloride (dielectric constant, 10.1 to 10.8) as it appeared probable that it would fulfil sufficiently well the above-mentioned requirements.

C.p. benzene (tested for the absence of traces of water) and a relatively pure grade of ethylene dichloride were used. The purity of the ethylene dichloride was of no consequence in so far as its dielectric constant was con-

cerned, as no assumptions were made in this respect. On the other hand, it was necessary to determine whether any of the slight impurities present might be adsorbed. It was demonstrated experimentally, however, that ethylene dichloride, benzene, or any of the impurities that might be present were not adsorbed on the cellulose to an extent that would influence the measurement of its dielectric constant.

TABLE I  
COMPOSITION OF SOLUTIONS

Solution	Wt. per cent		Solution	Wt. per cent	
	Benzene	Ethylene dichloride		Benzene	Ethylene dichloride
1	100.00	0.00	5	27.99	72.01
2	76.48	23.52	6	16.45	83.55
3	60.87	39.13	7	0.00	100.00
4	40.64	59.36	4a	31.01	68.99

#### Cellulose

The cellulose was prepared by the method for standard cellulose described by Argue and Maass (1).

#### The Dielectric Cell

The experimental condenser and its glass envelope formed the dielectric cell. The condenser consisted of two concentric brass cylinders, 0.07 cm. in thickness, 18 and 17 cm. in length, and 2.6 and 1.6 cm. in diameter, respectively. The outer cylinder was made longer than the inner one for purposes of shielding. The two cylinders were kept apart by two Pyrex rings, 0.5 cm. in thickness and 1.0 cm. in height. A vertical section 0.7 cm. wide was cut out of each ring to allow penetration of liquid into the inter-cylinder space. (The glass rings were made first and the brass cylinders chosen afterwards to fit them very tightly.) There were four small projections on the bottom of the outer cylinder, bent inwards, upon which one of the glass rings rested. About half a centimetre from the bottom of the inner cylinder there were four projections, bent outwards, which rested on the glass ring. The other ring was similarly placed at the top of the condenser. This arrangement prevented any movement of the two cylinders relative to each other. The assembled condenser was placed in the Pyrex envelope (*C* in Fig. 2) which was 3.2 cm. inside diameter and 35 cm. in length. The additional length of the envelope (over that of the condenser) was required in order that it could be sealed without heating the cellulose. Electrical connection was made to the cylinders by means of two fine copper wires, a section of each being replaced by a small piece of thin platinum foil, in order that a glass-to-metal seal could subsequently be made by the method of Campbell (4). These arms were placed as far apart as was conveniently possible (about 6 cm.) so that the lead capacity might be a minimum. It was necessary to

include the experimental condenser in the circuit in such a manner that the outer cylinder was grounded, in order to avoid a capacity effect between the condenser and the bath liquid. Under these conditions, the capacity of the empty condenser plus the leads was found to be the same (53.65 cm. on the capacity scale) whether or not the dielectric cell was surrounded by the bath fluid.

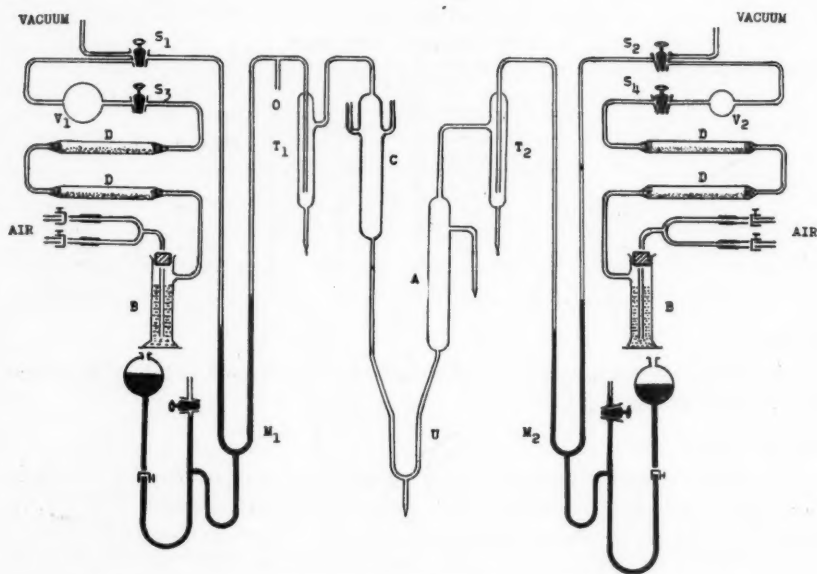


FIG. 2. Experimental set-up for measurement of dielectric constant of cellulose.

### *The Bath*

The dielectric cell was immersed in a Pyrex water bath. The liquid was stirred by means of compressed air forced through an O-shaped glass tube containing small openings, and placed at the bottom of the bath around the cell. The temperature of the bath could be lowered or raised by sending a stream of cold water or a mixture of steam and air through the stirrer. Small changes in temperature were made at times by simply adding small amounts of hot or cold water. The temperature of the bath could be easily kept within  $0.2^{\circ}\text{C}$ . of the desired temperature ( $25.0^{\circ}\text{C}$ .).

### *Experimental Procedure*

The combined capacity of the leads and the condenser filled with liquid was measured with each of the seven solutions. For this part of the work the tube coming from the bottom of the cell was not connected to the U-tube as shown in Fig. 2, but the lower end was left open so that the liquids could be drawn up into the cell. Inasmuch as it was necessary that the capacity of the leads be kept the same for this and subsequent measurements, the

platinum foil was included in the internal leads but the glass-to-metal seals were not made at this stage of the work. The fine copper leads were brought out of the arms of the cell through a cork and the seal was completed with DeKhotinsky cement. This was sufficiently air-tight since the cell was not subjected to a high vacuum at this stage.

By applying a vacuum through  $S_1$ , about 150 cc. of the liquid contained in a tall cylinder was drawn into the cell. Capacity measurements showed that it was necessary to raise and lower the liquid several times before the walls of the cylinders became thoroughly wetted. All measurements were made with the liquid at a given height, about 1 cm. above the top of the condenser. Small differences in the level of the liquid relative to this point could not be detected by capacity measurements since the capacity of the internal leads was quite small. Capacity measurements made at  $25.0^\circ \pm 0.2^\circ$  C. usually agreed within 0.10 cm. for successive measurements on the same solution. The average values for the capacity of the condenser filled in turn with the various solutions are given in Table II. The liquid was drained from the cell at the conclusion of each measurement and the cell swept with a current of air dried by means of the sulphuric acid tower *B* and the two phosphorus pentoxide tubes *D*, *D*. At the same time the bath temperature was raised to  $90^\circ$  C.

TABLE II  
CAPACITY OF CONDENSER FILLED WITH SOLUTION ONLY, AND WITH SOLUTION PLUS CELLULOSE

Solution	Capacity with solution only, cm.-units	Capacity with solution and cellulose, cm.-units	Solution	Capacity with solution only, cm.-units	Capacity with solution and cellulose, cm.-units
1	76.75	—	5	152.10	151.85
2	94.05	—	6	175.55	172.20
3	108.20	122.20	7	221.50	—
4	131.90	133.70	4a	147.00	147.05

The cell was next taken from the bath and the cellulose was packed into the condenser. It was only necessary to remove the upper glass ring from the condenser and pack cellulose into the inter-cylinder space. Considerable care was exercised in sealing the cell inasmuch as an excessive heating of the cellulose had to be avoided. The completed cell was replaced in the bath in its original position and joined to the rest of the apparatus in the manner indicated in Fig. 2.

It was first necessary to remove any water that the cellulose had adsorbed. The bath was left at room temperature and the system was evacuated through  $S_1$ , a Hy-Vac pump and a Langmuir diffusion pump being used. Evacuation was continued for three hours, and then the bath temperature was raised to  $100^\circ$  C. At the end of six hours evacuating at the higher temperature, the capacity of the experimental condenser had reached a constant value; this

indicated that the cellulose was thoroughly dried. With the system under vacuum and the bath temperature at 25° C., the capacity of the leads and the condenser containing the cellulose was found equal to 60.15 cm. Air, dried by passage through the two drying units, was then slowly let into the system until the pressure was atmospheric. The fact that no change took place in the capacity of the system following this operation showed that the air had been thoroughly dried.

The method of introducing the liquid into the cell filled with cellulose presented several difficulties. It was highly important that the system be under vacuum when this was carried out in order that the possibility of air bubbles being trapped among the cellulose fibres be reduced to a minimum. It was obviously impossible to use stopcocks. The difficulty was overcome by the use of frozen seals of the same composition as that of the liquid with which the cell was to be filled.

During the introduction of the liquid into the U-tube, precautions were taken that the moist air of the atmosphere did not come in contact with the cellulose. Compressed air was first introduced into the system by way of the drying unit shown on the left (Fig. 2). At the same time the sulphuric acid tower shown on the right was disconnected from the phosphorus pentoxide tubes in order to allow a point of exit for the air. The tip on the arm of *A* was then broken and a loosely stoppered test tube containing about 20 cc. of the liquid was placed under it. The supply of compressed air was shut off and the sulphuric acid tower again connected to the system. A Dewar flask containing solid carbon dioxide and acetone was placed around the trap *T*<sub>2</sub> to prevent the vapors of benzene and ethylene dichloride from passing through the Hy-Vac pump in subsequent operations. The freezing mixture was kept around the trap from this stage to the end of the run. Volume *V*<sub>2</sub> (about 50 cc.) was then evacuated. With *S*<sub>2</sub> closed, *S*<sub>4</sub> was partly opened. This caused the liquid to rise into the arm of *A* and finally to flow into the U-tube. When the arms of the U-tube were filled to a height of about 10 cm., *S*<sub>4</sub> was closed. The height of the liquid in the left-hand arm was finally adjusted to 5 cm. by introducing a slight amount of compressed air into this side of the system. A Dewar flask containing solid carbon dioxide and acetone was then placed under the tip of the U-tube, one centimetre of it being immersed in the freezing mixture. After the liquid had frozen, the freezing mixture was raised an additional centimetre. This process was repeated until all the liquid in the left-hand arm was frozen, after which atmospheric pressure was established on both sides of the frozen seal. All the liquid in the right-hand side of the U-tube was not frozen, in order that there would always be a supply ready to flow into the space resulting from the contraction that the liquid first underwent on freezing and then on reaching thermal equilibrium with the freezing mixture. It was not desirable to leave any liquid in the left-hand arm inasmuch as this side of the system was to be highly evacuated in subsequent operations.

After the frozen seal had been made, the vessel *A* (volume 300 cc.) was filled with the solution. A covered flask containing the solution was placed

under the arm and, by application of suitable vacuum at  $S_1$ , about 250 cc. of the liquid was drawn into the vessel  $A$ . The flask was then removed and a current of dried air was passed through the arm to remove as much as possible of the liquid remaining in it. Some difficulty was at first encountered in attempting to seal this arm owing to the fact that the charring of the liquids prevented the making of a good seal and also because the solutions were slightly inflammable. The difficulty was overcome by stoppering the arm and then gently heating before attempting to seal it.

The system to the left of the frozen seal was next evacuated for 5 to 10 hr.; the pressure was then usually about  $10^{-3}$  mm. of mercury. The pressure above the liquid in  $A$  was reduced to the vapor pressure of the liquid, a small amount of which was allowed to boil off in order to drive out as much air as possible. It was essential that the difference between the air pressures in the evacuated spaces over both sides of the frozen seal be as small as possible in order that the liquid might not be pushed beyond the dielectric cell on the subsequent thawing of the seal.

Care had to be exercised in thawing the seals since benzene and ethylene dichloride expand on liquefying. The seal was melted by lowering the freezing mixture a half a centimetre at a time until the arch of the U-tube was reached. At this point the melting of the solid was hastened by briskly rubbing the inner part of the arch with the fingers. Following the removal of the seal, the liquid rose into the dielectric cell but to a height never more than 5 cm. above the bottom of the condenser. The liquid was then raised to a height slightly below a given point (the same as that used in the previous set of measurements) by allowing air to expand from  $V_2$  into the space above the liquid in  $A$ . The finer adjustment in the level was made by raising the mercury in the mercury cut-off  $M_2$ . About half an hour was allowed for the liquid to reach thermal equilibrium with the bath before any capacity measurements were made. After the capacity of the system had been determined, the liquid was removed from the dielectric cell by applying a vacuum at  $S_2$ . Thus by alternate use of pressure and vacuum by means of which the cell was filled and emptied, a series of capacity measurements of the same solution could be made.

Several preliminary runs brought forth the following facts. The capacity of the condenser was found to successively increase during the first five or six times that the liquid was drawn out of the cell and sent in again. This indicated that at pressures as low as  $10^{-3}$  mm., the cellulose fibres trapped some air bubbles which were removed a few at a time. That all the air was not removed even when the capacity of the condenser had attained a constant value was shown by the fact that the "constant value" was not the same for an entirely independent set of measurements on the same solution. This showed that some of the air bubbles were difficult to dislodge and also that the number of this type that formed was not the same for different runs. It was accordingly necessary to modify the experimental procedure. Subsequent to the thawing of the frozen seal, the liquid was sent into the cell and

drawn out about ten times. After the liquid had been adjusted to the desired height, the frozen seal was again formed in the U-tube. Air was then let into the space above the liquid in the cell until the pressure was atmospheric. It was reasoned that any bubbles that had formed in the liquid at an air pressure of  $10^{-3}$  mm. would most certainly be reduced to a negligible size when the external pressure was increased to atmospheric. The results indicated that this was true. It was found that owing to the contraction of the air spaces subsequent to the establishment of atmospheric pressure above the liquid, the level dropped slightly. To offset this, the liquid was raised about the same distance above the proper level before the frozen seal was made. This was probably not necessary, since, as has been shown previously, the internal lead capacity was so small that a slight difference in the level of the liquid was of no consequence.

It was considered improbable that the dielectric constant of cellulose was as low as that of Solutions 1 and 2. Accordingly the series of capacity measurements was begun with Solution 3 and continued with solutions of higher dielectric constant until the point of intersection of the two curves previously mentioned was satisfactorily established. The average values of the capacity of the leads and the condenser filled with cellulose and each of Solutions 3 to 6 are given in Table II. Two runs were carried out with each solution, the separate capacity values agreeing well within 0.10 cm.

At the conclusion of a set of capacity determinations the liquid was drained from the cell by breaking the tip on the tube below the U-tube. Air was then passed through the cell by way of the left-hand drying unit. Considerable difficulty was experienced in attempting to seal the tube below the U-tube after the liquid had been drained from the cell. The cellulose held back a considerable amount of the liquid, and it dripped continuously into the U-tube. As mentioned previously, the charring of the liquid on strong heating prevented the making of a satisfactory seal. The difficulty was overcome by the use of a solid carbon dioxide trap. A piece of asbestos was wrapped around the glass tubing in the form of a cone just below the cell. This was filled with finely powdered solid carbon dioxide. Prior to making the seal, the open tube was closed with an asbestos-protected cork and the U-tube and connecting tubing was heated. Under these conditions a satisfactory seal could be made.

The liquid held back by the cellulose was removed by evacuating the system through trap  $T_2$  (surrounded with solid carbon dioxide and acetone). By a measurement of the capacity of the condenser, it was found that all the liquid was removed from the cellulose in three hours or less of pumping. At the end of this time, evacuation was stopped, and dried air was let into the system. The solid that collected in  $T_2$  was carefully thawed and removed by breaking the tip at the bottom of the trap.  $T_2$  was then sealed, a current of dried air passing through the apparatus from left to right during this operation.

It has been indicated elsewhere that experimental evidence was obtained to show that benzene, ethylene dichloride, or any of the impurities that

might be present were not adsorbed by the cellulose to an extent that would influence the measurement of the dielectric constant of cellulose. Before one of the capacity measurements in which the solution was sent into the condenser filled with cellulose only was taken, the part of the frozen seal immediately below the dielectric cell was allowed to melt. This caused the evacuated space to be filled with the vapors of the liquids. The system was allowed to stand thus for 30 min. The capacity of the condenser was then measured but no increase (over the normal capacity of the cell filled with cellulose) was found. This points to the absence in the solutions of any constituents that might be adsorbed in sufficient quantities to influence the measurements in this investigation.

It would have been impossible to carry out successfully the above experimental procedure without the inclusion of the mercury cut-offs in the system, as the vapors of the liquids had a tendency to attack the stopcock grease. The mercury in the cut-offs was accordingly kept raised at all times unless otherwise necessary. The presence of the mercury in the system is of no consequence as far as the measurements are concerned, as it has been shown by Russell, Maass, and Campbell (7) that mercury is not appreciably adsorbed by cellulose.

In Fig. 3 is shown the relation between capacity of the condenser and composition of the liquid for the sets of measurements in which (i) the condenser was filled only with the liquid (Curve 1), (ii) the condenser was filled with cellulose and liquid (Curve 2). The point of intersection of these curves was actually determined on a much larger graph than is given here, one on which the capacity measurements were plotted to the nearest 0.1 cm. and the composition values to the nearest 0.05%. The two curves were found to merge into one for a distance given by the capacity as 146.2 to 147.6 cm. and by the composition as 68.50 to 69.50%. The mean of these values, 146.9 and 69.00, respectively, was taken as the true point of intersection. A liquid of this composition was introduced into the cell, and a capacity value of 147.05 cm. was obtained; this agrees favorably with that given above.

The agreement between the value taken from the graph and the experimentally obtained value is no proof that this point is the point of intersection of the two curves. It indicates only the agreement that can be obtained between points taken off Curve 2 and the experimental values. To prove conclusively, however, that the value obtained for the point of intersection of the two curves was not far from the correct one, it was necessary to introduce the above solution into the empty condenser. (This solution will henceforth be termed Solution 4a.) The dielectric cell was therefore dismantled and the cellulose removed. It was replaced in the bath and the capacity of the condenser filled with Solution 4a was determined. It was found equal to 147.00 cm. (compared to 147.05 cm.). This shows definitely that the point previously chosen as the point of intersection lies on both Curves 1 and 2. (In other words, it indicates that no capacity change has been introduced in dismantling the condenser and again assembling it.) It was accord-

ingly necessary only to determine the dielectric constant of this solution in order to arrive at a value for the dielectric constant of cellulose.

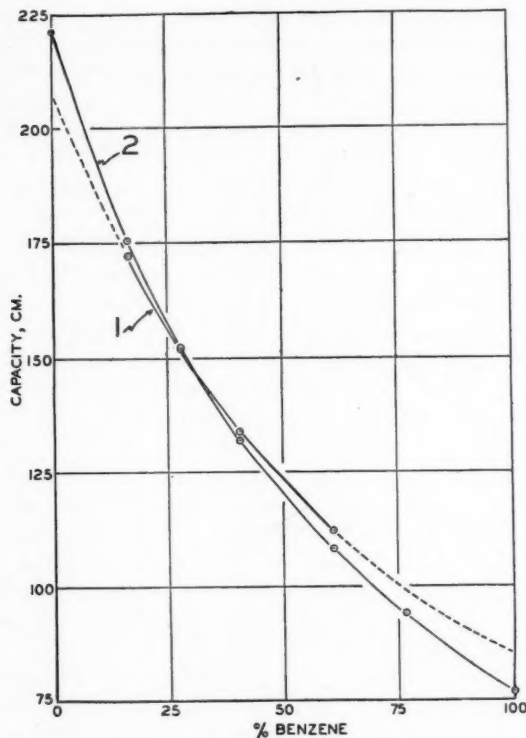


FIG. 3. Relation between capacity and composition. Curve 1, solution. Curve 2, solution plus cellulose.

#### Calculation of the Dielectric Constant of Cellulose

It has been mentioned that in calculating the dielectric constant from the capacity values experimentally determined, it is necessary to allow for the capacity of the leads. A value for the effective lead capacity was obtained by substituting in Equation (4) the value of the dielectric constant of benzene and the corresponding values of  $d_1$  and  $d_2$ . This gives:—

$$2 : 27 = \frac{76.65 - d_3}{53.65 - d_3}$$

whence  $d_3 = 35.45$ .

The accuracy of this calibration was tested by measuring the dielectric constant of chloroform, for which satisfactory agreement with the values in the literature was obtained.

Now, by use of the value of  $d_3$  and the above equation, all previous capacity measurements can be expressed in terms of the dielectric constant. These are given in Table III. These values have been plotted in Curves 1 and 2 of Fig. 4. The point of intersection gives directly the dielectric constant of cellulose. As was done previously these values were plotted on a larger scale than is shown here (to 0.01 dielectric units and 0.05%). The two curves

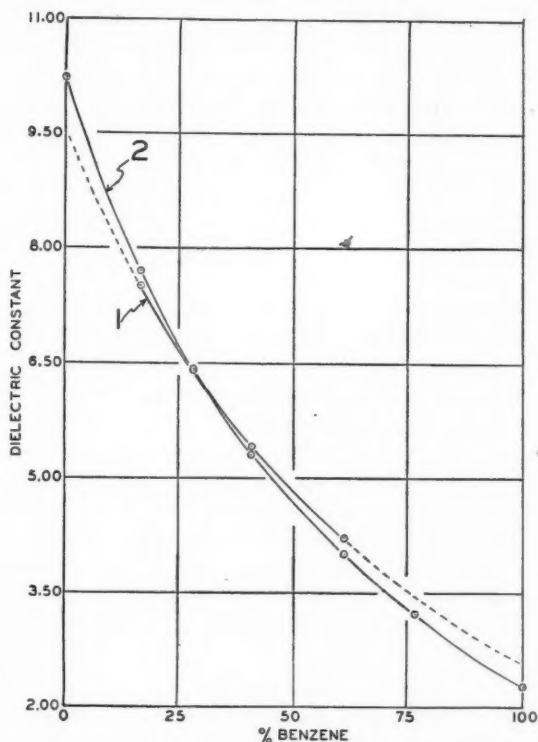


FIG. 4. Relation between composition and dielectric constant. Curve 1, solution. Curve 2, solution plus cellulose.

TABLE III  
DIELECTRIC CONSTANT OF SOLUTION ONLY AND OF SOLUTION PLUS CELLULOSE

Solution	Dielectric constant of solution only	Dielectric constant of solution and cellulose	Solution	Dielectric constant of solution only	Dielectric constant of solution and cellulose
1	2.27	—	5	6.41	6.39
2	3.22	—	6	7.70	7.51
3	4.00	4.22	7	10.22	—
4	4.30	5.40	4a	6.13	6.13

merged into one for a distance given by the dielectric constant as 6.07 to 6.17. The mean of these values, 6.12, was taken as the dielectric constant of cellulose.

It was shown previously that the condenser possessed the same capacity when filled with cellulose and Solution 4a as when it was filled with the solution only. By substituting this capacity measurement (147.05 cm.) in Equation (1), a value of 6.13 is obtained for the dielectric constant of cellulose.

### Discussion of Results

In the foregoing treatment of the subject, the values for the dielectric constant have been expressed to the nearest 0.01 unit. This has been done more to show the accuracy of which the method is capable rather than an attempt to measure the dielectric constant of cellulose to this value. It is quite probable that the dielectric constants of two samples of standard cellulose might differ by a number of times the above amount. Expressed to the nearest 0.1 unit, the value of this constant as found in this work is given as 6.1.

As mentioned previously, the literature does not contain a value for the dielectric constant of standard cellulose. It is stated in the International Critical Tables (5) that the value of  $\epsilon$  for cellulose lies between 3.9 and 7.5, but the source of these data is not definitely indicated. Campbell (3) obtained a value of 6.7 for a regenerated cellulose. Stoops (9) found the dielectric constant of cellophane (which is also a regenerated cellulose) to vary from 6.7 to 7.7, the value depending on the frequency of the measuring current. The dielectric constant of standard cellulose would be expected to be different from that of a regenerated cellulose inasmuch as the treatment employed in the production of the latter alters the crystal structure. On the other hand, it is felt that in the light of the values obtained by Campbell, Stoops, and the writers, the value for the dielectric constant of cellulose should be given within smaller limits.

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